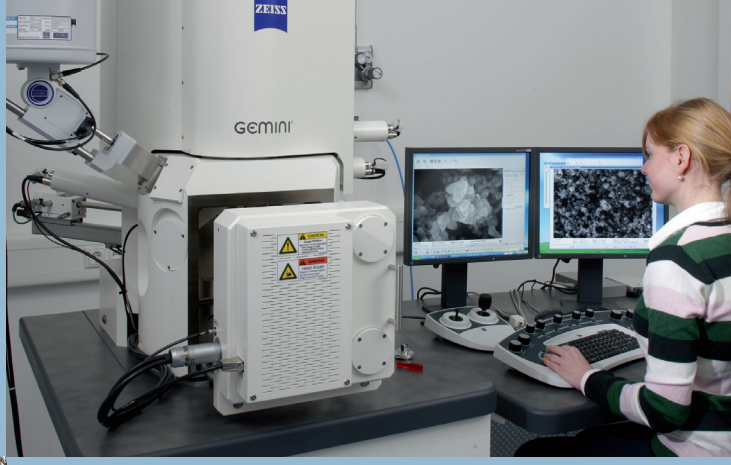

IEF-3 Report 2009

Basic Research for Applications

Mitglied der Helmholtz-Gemeinschaft

JÜLICH
FORSCHUNGSZENTRUM

Schriften des Forschungszentrums Jülich
Reihe Energie & Umwelt / Energy & Environment Band / Volume 45

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IEF-3 Report

Basic Research for Applications

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Reihe Energie & Umwelt / Energy & Environment Band / Volume 45

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Preface

In terms of quality, the years 2007 and 2008 were characterized by the considerable extension of our laboratory capacity. The fuel cell laboratory, which is dedicated to analysis and thus strategically enhances IEF-3 activities in the area of basic research, was opened just before Christmas 2008 after we succeeded against the odds in attracting qualified personnel in what is a rather restricted labor market. At this time, laboratory activities were focused on what is known as the structure-activity relationship, which involves explaining the mechanisms in electrochemically active and catalytic structures in membrane electrode assemblies for fuel cells and in catalytic structures for reforming. Studies focus on the three-dimensional construction of the layers with their various components and how they function in detail. With regard to soft materials used in low-temperature fuel cells, apart from the actual analysis – such as scanning electron microscopy – the preparation of samples is also particularly important. This was taken into account when equipment was being acquired. The fuel cell laboratory also provides the experimental basis for the verification of computer models for electrode layers. This will see the experimental platform for modeling go beyond the already existing verification of fuel cells on a pilot scale into the area of basic research. The fuel cell laboratory was made possible as a result of an expansion investment from the Helmholtz Association of German Research Centres (HGF), to whom we would like to express our gratitude here.

Closely connected to this is the technical side of the fabrication of membrane electrode assemblies, which can only be reproducibly fabricated using large-scale equipment. After years of experience working with a partially automated coater, we successfully acquired third-party funds in 2007 for a fabrication facility, which was then erected in 2008. This facility allows gas diffusion electrodes to be fabricated in a number of different ways, fuel cell membranes to be directly coated, and electrode layers to be specially structured so that models can be verified. In combination with the fuel cell laboratory, this excellent technical equipment for the preparation stage will allow the structure-activity relationship to be explained in a targeted manner. We would like to thank the Federal Ministry of Economics and Technology in particular for providing financial support for the fabrication facility.

As a result of the good long-term findings regarding reforming, it was deemed necessary to modify and upgrade the tank infrastructure for middle distillates in 2007. This infrastructure was set up in 2008 and it is hoped that it will go into operation in the first three months of 2009. This aim is not only to allow long-term tests with a constant fuel quality for large storage quantities but also basic tests with different types of fuel, such as bio-to-liquid (BTL) fuels, which will be made possible by the option of storing a total of eight fuel qualities.

The reforming technology is currently being transferred to a SME within the framework of a project coordinated by the Ministry of Economics of the state of North Rhine-Westphalia. One of the company’s strengths lies in the fabrication of complex metal sheet structures and weldments. The transition to sheet metal led to a reduction in the fabrication costs as well as further improvements in the technical properties of the reformer in dynamic operation.

A significant breakthrough was made in the desulfurization of liquid fuels. We succeeded in identifying two procedures that allow kerosene to be desulfurized in small decentral facilities

in an energy-efficient manner and to observe the limit that is currently permissible for diesel at gas stations, namely 10 ppm S. These promising approaches will be expanded using a systems technology methodology.

Having created a promising foundation over a number of years on a small scale, a new group was set up and expanded in 2008 for the high-temperature polymer fuel cell. The group's main aim is to develop stacks for on-board power supply run on reformate.

With regard to the SOFC, stacks were operated successfully for the first time for up to 10,000 hours with little degradation. A new coating developed at IEF-1 did not display any visible degradation in a test when operated for 3,500 hours.

It was particularly encouraging to read an article in the press near the end of the year dedicated to basic research on the direct methanol fuel cell. In the Citation Index, Forschungszentrum Jülich appeared directly after Princeton University with an average of more than thirteen citations per article. Jülich therefore ranks as the best among German institutions involved in energy research. This result was made possible by work conducted at the Institute of Photovoltaics and the Institute of Fuel Cells in the area of the DMFC. In both cases, it proves how fruitful a good combination of basic and applied research can be.

After a year of extensive modifications and expansions, we see 2009 as the year in which we will set off to explore new fields of research. This process will be largely supported by a proactive consolidation of the new institutions that have been created.

Jülich, October 2009

1

Expansion

Investments for the Expansion of Research Infrastructure

- Physicochemical fuel cell laboratory: new methods of resolving structure activity relationships in complex multilayers
- Component and system test facility: extensive resources for investigating the operating characteristics of components and systems for fuel processing
- Research and development facility for new fabrication techniques: Coating and assembling under industrial conditions

1.1 Physicochemical fuel cell laboratory: new methods of resolving structure activity relationships in complex multilayers

1.1.1 Initial situation and objectives

Despite the approaching commercialization of fuel cell technology, for example, in niche markets, a strong demand has recently re-emerged for basic mechanism-oriented research. Analytical methods have become increasingly important in this respect, as a result of significant improvements in resolution and variability.

This approach will be followed by exploiting the potential associated with the new equipment in the physicochemical fuel cell laboratory, which was financed through an HGF investment. The laboratory is mainly equipped to deal with the direct methanol fuel cell (DMFC) and the high-temperature polymer electrolyte fuel cell (HT-PEFC). In the period under review, a new building complex was constructed for the analysis laboratory and a large proportion of the equipment required was evaluated, selected and purchased on the basis of its efficiency for the development of the above-mentioned fuel cell types.

Analysis work concentrates on investigating the structure and physicochemical properties of functional layers and the spatially resolved characterization of fuel cell components for DMFCs, HT-PEFCs and reformers. One of the crucial aspects for imaging the microstructure of low-temperature fuel cell components is the artifact-free sample preparation of fragile, wet polymers. The main fields of research are:

- the elucidation of the influence of structure on the properties and performance of fuel cell components
- the elucidation of the degradation mechanisms of DMFCs and HT-PEFCs
- the study of oxygen reduction on HT-PEFC cathodes

The aim is to gain a deeper fundamental understanding of the physicochemical processes in fuel cell components, and to use this understanding to develop measures to increase their performance and reduce degradation phenomena.

1.1.2 Specifications of the installed equipment

The main device for imaging structures that sometimes reach the nanometer scale is a field emission scanning electron microscope (FE-SEM) manufactured by Zeiss with a connected energy-dispersive X-ray spectroscopy (EDX) system manufactured by Oxford Instruments. In addition to its well-known excellent resolution, the Zeiss Ultra offers high variability in terms of the materials to be investigated.

The latter is achieved by an innovative gas injection system that prevents the charging of non-conducting samples (charge compensation system). In this system, nitrogen is guided directly onto a limited local area of the sample via a gas injection needle. This only marginally impairs the vacuum in the test chamber, so that the in-lens detectors, which are indispensable for high resolution, can be used in an unrestricted manner even when the charge compensation system is employed.

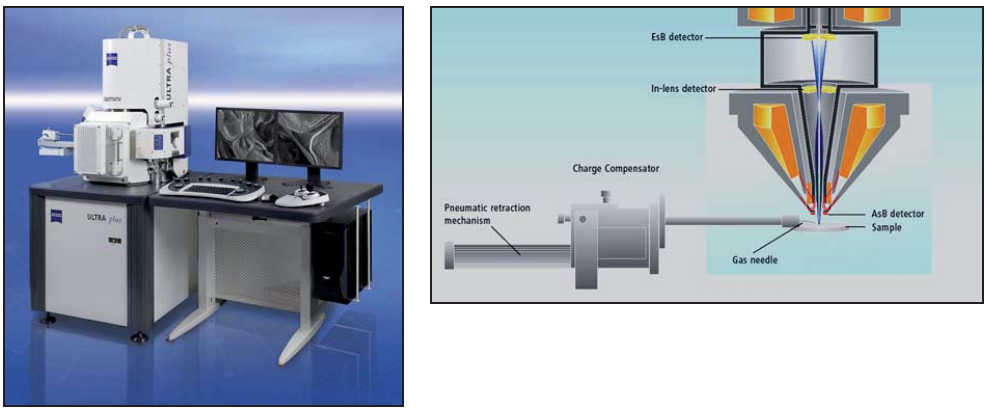


Fig. 1: **Zeiss Ultra plus field emission scanning electron microscope and schematic diagram of the charge compensation system**

For the imaging of suitable sample materials, a number of complementary preparation methods were evaluated and the equipment required purchased. For classic “metallographic” preparations for the fabrication of transverse sections, for example, complete membrane electrode assemblies, the following devices manufactured by Struers are available:

- Precision cut-off machine (Fig. 2) — Accutom 50
- Vacuum impregnation unit — Epovac
- Hot mounting press — CitoPress-1
- Manual grinding machine — LaboPol-2
- Automatic grinding and polishing machine (Fig. 2) — TegraPol-21 + TegraForce-5

Fig. 2: **Struers Accutom 50 precision cut-off machine (left) and Struers TegraSystem grinding and polishing machine (right) used to prepare samples**

For the analysis of “free standing” membranes or membranes with applied catalyst layers, thin sections can be produced using ultramicrotomy. In principal, such ultrathin sections can be analyzed in a transmission electron microscope. However, in IEF-3, they are initially analyzed using light microscopy and scanning electron microscopy. An advantage

associated with this method is the low volume of excitation for EDX measurements, which leads to a very good lateral resolution.

Another innovative sample preparation technique is ion beam preparation (Fig. 3), which is used to prepare reproducible mirror-like cross sections of MEAs. A cross section polisher manufactured by Jeol was acquired for this purpose. This machine prepares cross sections of heterogeneous coating systems of any roughness and porosity as well as materials with varying hardness. The relatively low beam current of the argon ion beam excludes almost all damage to the sample surface. Furthermore, this technique allows relatively large samples to be prepared, although long processing times are required.

Fig. 3: Jeol Cross Section Polisher ion beam preparation system

An enhanced use of spatially resolved measurements in the analysis laboratory is therefore important because the inhomogeneous distribution of media in fuel cell stacks causes uneven current distribution. This not only decreases the stack performance, but locally higher current loads also cause strong degradation of cell and stack areas and can lead to failure of the whole system. Spatially resolved methods make it possible to study local effects such as current density, impedance and temperature in operando. These findings can then be used to identify favorable performance characteristics, material parameters and designs, which enable the homogeneous distribution of media in fuel cell stacks and thus facilitate improved performance and lower degradation rates. In close cooperation with the Helmholtz Centre Berlin (HZB), these methods were combined with externally available in operando methods, such as neutron radiography for the determination of water and gas distribution (Chapter 4.1), which led to a further increase in the knowledge gained.

The spatially resolved methods available in the fuel cell laboratory comprise segmented cell technology (SCT), magnetotomography (MT), and spatially resolved mass spectrometry (SRMS).

SCT is an electrochemical method, which allows the current and impedance distribution to be measured on the active surface of a PEM fuel cell. The method is based on circuit board technology with active compensation of the ohmic voltage drop and was developed by the

Institute for Power Electronics and Electrical Drives (ISEA) at RWTH Aachen University in cooperation with Forschungszentrum Jülich. The process is characterized by a high signal-to-noise ratio and a large frequency domain. This allows local impedances to be measured in addition to the spatially resolved determination of current densities. A 4-to-1 multiplexer (ISEA “EISPlex”) combined with the ISEA “EISMeter” galvanostat permits the fast measurement of up to 56 segments. Temperature sensors on the adaptor circuit board also allow the temperature distribution to be determined over the surface of the cell. The SCT is variable with regard to the design of the test cell and the flow field plates. Up to now, spatially resolved measurements have been performed using SCT on test cells with electrode areas between 3 cm² and 18 cm². However, stack MEAs with an electrode surface of 320 cm² are also to be studied this year. Fig. 4 shows the SCT measuring apparatus and, as an example, one of the test cells used.

Fig. 4: **Measuring apparatus (left) and test cell (right) for the spatially resolved measurement of current densities and impedances (SCT)**

Magnetotomography is a non-invasive technique currently being developed to measure the current distribution in a fuel cell. The method is based on measurements of the external magnetic field, which is generated by the interior flow of current. The magnetic field in this case is used like a “fingerprint” of current distribution. The external magnetic field is recorded using two triaxial magnetoresistive sensors.

The relationship between magnetic field data and current density is described in general by Maxwell’s equations. The reconstruction of current density from the magnetic field is carried out using the Biot Savart operator

$$H(x) = \frac{\mu_0}{4\pi} \int_{\Omega} \frac{x - y}{|x - y|^3} \times j(y)\, dy$$

and the Tikhonov regularization for stabilization.

The advantage of magnetotomography is that measurements can be taken without physical contact. In other words, no measuring instruments are inserted into the fuel cell, which significantly reduces the measurement effort. The magnetotomograph is shown in Fig. 5.

Fig. 5: **Magnetotomograph based on a positioning system including two magnetic sensors (Honeywell HMC 1063)**

Spatially resolved mass spectrometry (SRMS) was developed at the University of Bochum by the working group headed by Prof. Muhler and Prof. Schuhmann, and adapted within the framework of a cooperation with Forschungszentrum Jülich for application on fuel cell components. This method is based on a heterogeneous, non-electrochemical reaction of a suitable gas with the catalyst in the electrode layers and the analysis of the product gas using a mass spectrometer. For electrodes with a platinum catalyst, the oxidation of methanol to carbon dioxide, for example, can be exploited. With the aid of a positioning unit, a capillary bundle in x/y direction is moved over the surface and the distance to the electrode surface is set in the z direction (Fig. 6). The reactive gas mixture is injected into the inner capillary, while in the outer capillary, the product gas is transferred to the mass spectrometer. In this way, the distribution of local activity can be automatically determined over an electrode surface. This is particularly interesting for studying local degradation effects on stack MEAs.

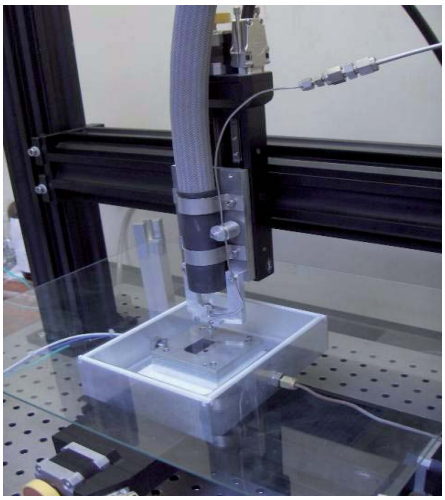


Fig. 6: **Spatially resolved mass spectrometry (SRMS); photo: N. Li, PhD thesis, University of Bochum 2007**

In addition to spatially resolved analysis techniques, expanded conventional measuring methods are also employed. From the field of thermoanalysis, these include thermogravimetry (TG) (Fig. 7, left) and differential scanning calorimetry (DSC) (Fig. 7, right), for the determination of mechanical properties, a tensile testing machine with climate chamber (Fig. 8) and a porosimeter (Fig. 9), and for the rheological determination of catalyst inks, a particle size measuring device. In order to explain degradation influences, a climate chamber and an environmental test chamber with a volume of more than 500 l each are available.

Fig. 7: **Thermoanalysis unit (TG) (left) and differential scanning calorimeter (DSC) from Perkin Elmer (right)**

In order to determine the decomposition behavior of MEA materials, thermogravimetrical analysis (TG and/or TGA) are mainly used. The materials can thus be thermally loaded from room temperature to 1,000 °C in different atmospheres. Only small amounts of material are

required for this, as the measuring system has a mass resolution of 100 ng. The maximum permissible total weight of 1.5 g means that highly precise weighing is possible. These measurements will provide detailed information on the amount of water taken up and the decomposition processes that occur. In addition, differential scanning calorimetry (DSC) with real power compensation can be applied. Using the available device (Perkin Elmer, Waltham, Massachusetts, USA), phase changes such as the glass transition temperature or the crystallization point can be determined in the temperature range of -130 °C to +600 °C on the basis of their heat release or uptake. It should be emphasized that a heating rate of up to +500 K/min can be applied. On the one hand, this allows the determination of phase transitions with low heat of reaction, while on the other, experiments can be conducted under practically relevant aspects, which for example take water stored in the material into account. The materials can thus be conditioned for measurements in a climate chamber under different climatic conditions. It is possible to set a temperature in the range of -40 °C to +180 °C and simultaneously control the humidity with a dew point between -12 °C and +70 °C or rather set a relative humidity of 10 % and 98 %. This makes it possible to determine degradation effects on MEA components, as well as to prepare samples for measurements with realistic climatic conditions under which a fuel cell actually operates.

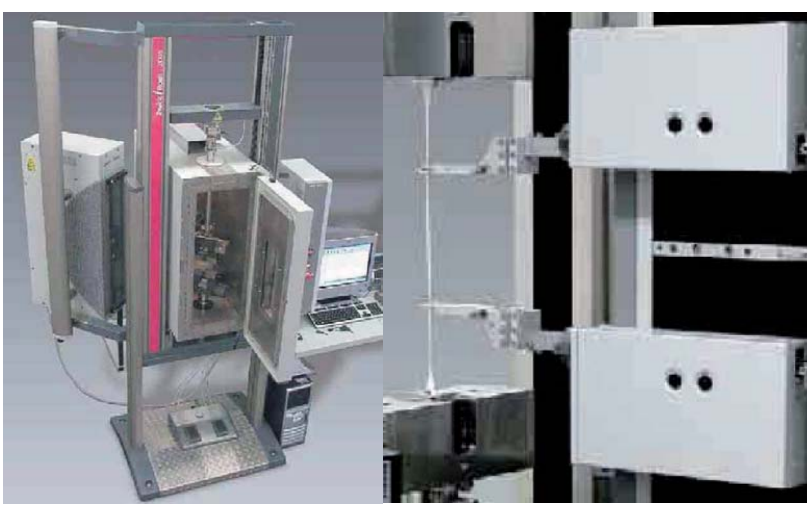


Fig. 8: **Material testing machine with climate chamber and mechanical strain gauge from Zwick GmbH**

In addition to determining the thermodynamic data of MEA components, their mechanical properties under operating conditions are just as important for the development of stacks and systems. For this purpose, we have a material testing machine (Zwick GmbH & Co. KG, Ulm, Germany) with a tensile load of up to 5 kN and a force resolution of 15 µN, equipped with a climate chamber. The special feature of this machine is that the humidity can be set with dew point temperatures of up to 65 °C, while the sample can simultaneously be exposed to temperatures between room temperature and +160 °C. This makes it possible to acquire information on technically relevant parameters, such as tensile strength, stiffness and creep under realistic conditions.

In order to gain information on the pore distribution of gas-permeable materials, such as the gas diffusion layer, a standard porosimeter manufactured by Porotec was purchased. The measuring technique applied was developed by Prof. Y.M. Volfkovich (Russian Academy of Sciences, Moscow, Russia). In contrast to conventional mercury porosimeters, this device uses liquids such as octane or water for pore analysis. This allows repeat measurements to be carried out on samples that have already been used. Furthermore, unlike mercury porosimetry, this method does not require high pressure to analyze very small pores, which means that the pore structure of the material being examined is only slightly affected during the measurement. The identifiable pore diameters range from macropores with diameters of several hundred micrometers to nanopores that are only a few nanometers in size. The measurements are fully automatic and the range to be analyzed can be adapted to the desired pore size.

Fig. 9: Drying chamber with weighing unit and robot in a standard porosimeter (Porotech, Canada)

Pastes are characterized using “Nanophox”, which is a device based on photon cross correlation spectroscopy (PCCS) manufactured by Sympatec GmbH (Clausthal-Zellerfeld, Germany) that measures particle size (Fig. 10). The liquid to be studied is illuminated by a laser and the scattered light from a small volume, typically of the order of 30 µl, is analyzed under an angle of 90 °. One of the advantages of this technique is that the low volume of excitation also allows cloudy solutions to be analyzed. Furthermore, this device is capable of measuring particles with magnitudes ranging from 10 µm to almost 1 nm. This makes the device particularly suitable for characterizing catalyst inks.

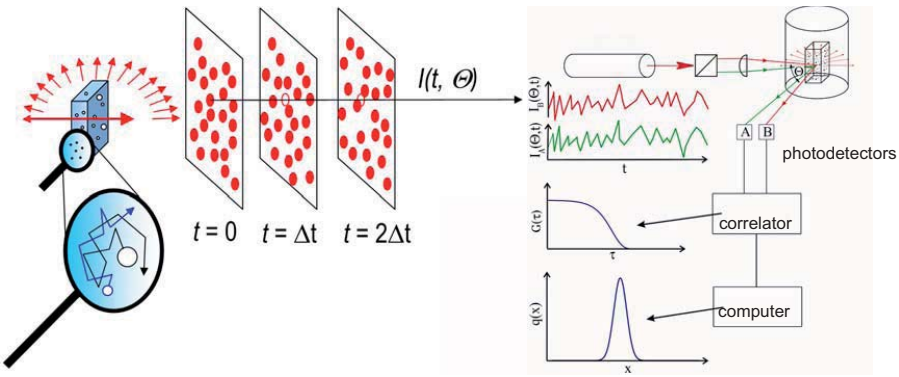


Fig. 10: Mode of operation of photon cross correlation spectroscopy

In addition to analysis methods, which are mainly designed for microscopic to macroscopic samples, an environmental simulation chamber (Binder GmbH, Tuttlingen, Germany) was purchased (Fig. 11). It has a capacity of more than 700 l and is therefore suitable for both fuel cell stacks and systems. The chamber is equipped with four sealable access ports and can be operated at a temperature range of -30 °C to +180 °C. Stacks and fuel cell systems can therefore be degraded, thermocycled and tested under non-laboratory conditions.

Fig. 11: Environmental simulation chamber (Binder GmbH, Germany) with a demonstration DMFC stack

1.1.3 Outlook

Until the analysis laboratory is fully functional, it will concentrate on meeting requirements for in-house studies. An example of a central topic is the degradation in DMFC stacks caused by

ruthenium corrosion. In the medium term, investigation methods will be refined in order to allow independent, basic research to be pursued on relevant topics in a targeted manner.

The combination of classic established studies such as performance assessments of single cells on the one hand, and the excellent potential associated with numerical simulations and modeling on the other hand, with the additional analytical post-investigation potential now available in the physicochemical fuel cell laboratory increases the attractiveness of IEF-3 with regard to acquiring third-party funds and establishing cooperations with or without industry participation.

1.2 Component and system test facility: extensive resources for investigating the operating characteristics of components and systems for fuel processing

1.2.1 Initial situation and objectives

With regard to a limited number of test facilities in the past for components (reformer, catalytic burner, water-gas shift reactor) and systems for fuel processing in the diesel laboratory, the laboratory infrastructure and the storage options were expanded to include a variety of fuels. In the past, it was only possible to test single reformers in time-limited continuous operation, at start-up and in dynamic load operation with selected individual fuels. System testing of a number of components for fuel processing together with a fuel cell was not possible in the existing laboratory environment in the past. Furthermore, the use of the energy carrier kerosene demanded a significant increase in safety precautions in the laboratory area. For a number of years, all test rigs have been analyzed by several methods for example in a FMEA and they have finally been CE certified. These analyses were then used as a basis to derive necessary safety measures in the laboratory for the testing of reformers and fuel cells. At IEF-3, primary explosion protection is applied. A prerequisite for this, however, is that the gases that could escape actually reach the sensors installed as safeguards in order to ensure primary explosion protection. With regard to the use of kerosene, particular care and attention is required. This means that in order to monitor a conventional test rig, two to three kerosene sensors must be installed in the base of the rig, because kerosene collects at the bottom when it is discharged in the steam phase. In the case of hydrogen, suitable sensors must be installed on the ceiling of the experimental hall and at the top of the test rig.

Another boundary condition is that the test facilities have been designed to be more flexible in the future. All test rigs are designed as modules. These modules are based on system profile frames, they are on wheels, and they can be attached via flexible corrugated tubes made of stainless steel to the gas and liquid supply systems in the laboratory infrastructure. Only the waste-gas lines are hooked up to the flue system via fixed pipe connections due to safety regulations. This allows individual test modules to be exchanged quickly in the laboratory environment. This is particularly effective when a module or its components are tested in a laboratory and technical modifications are carried out to the system or the components in another module in a different place. When work is complete, the modules can then be exchanged.

1.2.2 Specifications of the installed equipment

The building work conducted can be divided into two areas: the newly constructed fuel storage facility and the provision of test boxes. As the two areas are not located in the one place, an appropriate infrastructure is required to connect them.

The fuel storage facility consists of one 25 m³ tank, two 2 m³ tanks (Fig. 12) and five 1.3 m³ tanks (Fig. 13). Furthermore, 96 barrels with a volume of 200 l can be stored in two barrel compartments. The following can be kept in the fuel storage facility: isoparaffin, n-paraffin, petroleum, white spirit, solvent naphtha, xylol, toluene, gasoline, kerosene, diesel fuel, extra light (EL) heating oil and so-called gas-to-liquid (GTL) and bio-to-liquid (BTL) fuels. The tanks

are located on a site licensed in accordance with the Water Resources Act (WHG). This site has a drain for any fuel that leaks as well as an oil separator. The volume that can be collected by the drain is 4.5 m³. All tanks can be filled using barrels (Fig. 14). The barrels are transported to the filling station by a suitable forklift and the contents then siphoned into the tanks using pumps in accordance with the safety regulations. The 25-m³ tank can also be filled via a tanker truck. An area has been accordingly licensed for this purpose.

Fig. 12: 25-m³ tank (in the background) and the two 2-m³ tanks on the licensed area

Fig. 13: Five 1.3-m³ tanks for storing different grades of diesel and kerosene

Fig. 14: Tanking process from a 200 l barrel

This allows eight different liquid hydrocarbons to be used for test operation and other fuel grades to be kept in the barrel compartments. Studies are currently concentrating on the following grades: premium diesel, low-sulfur kerosene, and an alkane mixture free from aromatic hydrocarbons.

The fuel storage facility is connected to the test boxes via eight fuel lines. Furthermore, nitrogen, air, hydrogen, carbon monoxide, carbon dioxide, methane and argon are fed into the test boxes from the gas store. In addition, a deionized water supply and cooling water supply have been installed. Boxes 1 – 4 have a surface area of 12 – 29 m^2. They can accommodate modules with a fuel processing system and/or a catalytic burner (box 1, see Fig. 15), component modules for reformers or a water-gas shift reactor (boxes 2 – 3) and systems including HT-PEFC stacks (box 4). All boxes have coupling systems so that the modules can be connected to the supply and removal systems. The waste gases from catalytic burners must be disposed of, as must the product gases of reformers in the single test rigs and the waste gases from fuel cell stacks. A distinction is made here between combustible residual gases from reforming and combustion gases, which ideally only contain nitrogen, carbon dioxide, water vapor and small quantities of residual oxygen. Furthermore, when these gases are cooled down, condensates are produced which must be removed separately. All boxes are equipped with gas sensors for hydrogen, carbon monoxide and kerosene as well as a ventilation system. If the system is shut down by a gas alarm, then only the box which triggered the alarm is affected. The waste-gas system has a maximum load that is equal to a H_2 capacity of approx. 30 kWth (lower heating value for hydrogen) per box.

Fig. 15: Internal installations in box 1

1.2.3 Outlook

The restructuring of laboratory capacities and the setting up of the fuel store allows IEF-3 to conduct different experiments on fuel processing in four different test boxes and the coupling of the system with the HT-PEFC. This enables component development, long-term experiments, and system tests with and without fuel cells to be pursued in parallel (Fig. 16).

Fig. 16: Module capable of accommodating a 7-kW_e reformer

1.3 Research and development facility for new fabrication techniques: Coating and assembling under industrial conditions

1.3.1 Initial situation and objectives

The development of automatic production processes for cell and stack components is indispensible for the targeted further development of fuel cells aiming towards commercialization and an increase in quality. IEF-3 has been pursuing this approach for more than seven years with visible success both in the case of the direct methanol fuel cell (DMFC) and in its initial activities on the high-temperature polymer electrolyte fuel cell (HT-PEFC) within the framework of a BMWi-funded project. Over the last few years, for example, IEF-3 has constructed, operated and further developed facilities for the continuous automatic fabrication of cell components such as gas diffusion layers (GDLs), gas diffusion electrodes (GDEs), membrane electrode assemblies (MEAs), distribution structures and bipolar plates (BiPs), as well as facilities for assembling cells and stacks.

At the end of 2001, IEF-3 purchased a coating machine (desk coater), which can be used to fabricate diffusion layers and catalyst layers for fuel cells on a continuous basis with mechanized application methods. A coating technique was developed using the desk coater, which allows diffusion layers with lengths of up to 50 m to be mechanically fabricated continuously from roll to roll. These layers are comparable to gas diffusion layers fabricated according to standard laboratory methods both in terms of their functionality as well as their layer structure. Catalyst layers for PEFCs and DMFCs with lengths of up to six meters were also fabricated in a continuous process using the desk coater by knife coating onto the diffusion layer and they have been successfully tested. The reproducibility of the batches was much better than for manual tests on a laboratory scale.

In the area of DMFC stack development, IEF-3 boasts specialist expertise in terms of realizing high-performance DMFC stacks and systems of the kW class. The ultimate aim is to systematically optimize performance and efficiency and to make competitive systems a reality. Within the framework of the fabrication and assembly techniques, the emphasis lies on work related to precisely manufacturing and assembling MEA, cell and stack components as this is the only way to improve the reliability and lifetime of fuel cells. For the reproducible fabrication of stacks, material testing must be improved, the components used must be monitored and checked regularly, and the fabrication techniques must be automated. Automating the production technology will lead to a reduction in the total costs of stacks.

In order to expand the methodological and technical options in the DMFC and HT-PEFC fields in terms of automated fabrication techniques for MEA and cell components as well as the automated assembly of stacks, and deal with the challenges associated with MEA component development on the one hand and stack development on the other, investments were acquired from the Federal Ministry of Economics within the framework of a project aiming to set up a pilot fabrication facility.

In combination with the further development of fabrication techniques and scientific analysis, which is being set up in parallel in IEF-3 thanks to project funding from BMBF, and a corresponding quality control, a pilot research and fabrication facility is being constructed which will allow the targeted development of different fabrication techniques from the raw material right up to the finished fuel cell stack. This facility will make a significant contribution

to fuel cell development within the framework of future industry cooperations and R&D projects.

1.3.2 Specifications of the installed equipment

The project is divided into two subtopics: fabrication techniques for MEA and stack components with a pilot facility and a number of laboratory scale facilities, and the assembly of MEA stacks.

1.3.2.1 Fabrication techniques for MEA components

The new coating facility is composed of different machines for the fabrication of electrodes on gas diffusion layers, membranes or transfer films by means of different processes. This diversity of methods is absolutely essential in order to fully understand and systematically further develop MEAs. The composition of pastes or inks, the application method and the substrate on which the paste or ink is to be applied have a considerable influence on the finished electrodes. They can largely be investigated independently of each other using the combination of equipment that is now available. Furthermore, for characterization, it is often useful not to analyze a complete membrane-electrode assembly (MEA) but to focus instead on single layers, because all layers in an MEA interact with each other, which makes it difficult to determine what layer causes what effects.

Flexible line coater Click&Coat

As an alternative to the existing desk coater coating system, a flexible line coater (Click & Coat) was installed. The “click” system does not just allow the necessary modules to be joined together and a complex coating process to be conducted in one run, but also enables individual process steps to be selectively investigated and optimized. Different coating units, for example, can be exchanged for other units while the other conditions remain unchanged. Additional process steps can also be integrated as required (Fig. 17).

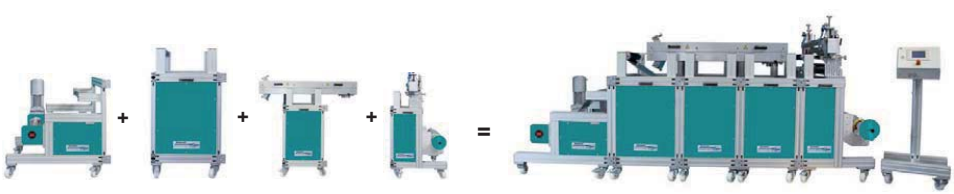


Fig. 17: Operating principle of the line coater “Click&Coat” (image courtesy of Coatema)

Moreover, in addition to carbon cloth and carbon felt, bending-resistant carbon paper and plastic substrate (for the fabrication of MEAs using the decal process) can also be coated. A cutting module at the end of the machine allows layers to be cut off and stored flat where rolling could lead to disadvantages in terms of quality in certain cases. There is also an option of integrating a robot in order to transfer the cuttings to a process involving custom-fit stamping.

The modules required for different production and development activities were defined in cooperation with the manufacturer. The following modules are available for use:

- Coiling modules: 2 single winders, 2 single unwinders, 1 double winder for use at the start of the machine, 1 double winder for use at the end of the machine, 1 edge control for forward mode, 1 edge control for reverse mode, 1 cutting module for use at the end of the machine
- Coating modules: 1 module for impregnating the material, 1 module for coating the material with a universal coating unit, on which coating heads can be mounted for blade coating and slot die casting (Fig. 18, right)
- Thermal treatment: 1 hot-air drying section with 3 separate adjustable temperature zones, each with a drying section of 1.5 m, 3 sintering modules, each with 1-m sintering sections, 1 cooling module with a 1 m cooling section, 1 calender module with heatable rolls
- Control system: 2 control terminals, which can be connected at the beginning and end of a long system, but which also allow the parallel operation of 2 systems
- Specifications: material width of up to 0.5 m, material speed of 0.1 m/min to 1 m/min, drying temperature of up to 235 °C, sintering temperature of up to 400 °C

Fig. 18: Click&Coat combination for the fabrication of gas diffusion layers (left), coating system slot coating (right)

The system is therefore suitable for both development work, which aims to reveal as much as possible about coating performance using as little material as possible, and for the fabrication of components for prototypes with the ultimate aim of coating large surfaces in as short a time frame as possible. The fabrication of small series is also possible and can be used to design suitable systems for series production in cooperation with industrial partners. The high drying temperatures make the system suitable for coatings for both the DMFC as well as the HT-PEFC.

After the coating system was put into operation (Fig. 18, left), work then began on transferring the coating technique developed on the preceding desk coater system to the new system and simplifying it by setting up the system specifically for the pending coating task. For example, in the past, four runs on the machine were required for hydrophobisation, sintering, coating with carbon paste, and sintering once again. Between each step, the material speed and the pathway of the material in the machine had to be changed. Now, only

two runs through the machine are required and the path of the material in the machine does not have to be changed. In addition to the time saved, which is extremely important for an industrial production process, this also decreases the danger of operating errors and therefore leads to better quality and reproducibility. The large number of coating parameters, which can be adjusted electronically and recorded using the control terminals, serve the same purpose. They allow the coating process to be documented in full. In the near future, work will begin on the development of new coatings using the slot dies as coating units (Fig. 18, right). Using the slot dies for coating has the advantage that the deposited amount of paste does not depend on the absorbency and evenness of the substrate, as is the case for knife coating. Instead, it depends solely on the amount added and the web speed.

Laboratory coating units

Two different concepts exist today for the fabrication of MEAs: (i) fabricating gas diffusion electrodes (GDEs) and pressing them with the polymer electrolyte membrane, and (ii) fabricating catalyst coated membranes (CCMs) and pressing them with gas diffusion layers (GDLs). While GDE fabrication is relatively well mastered and has been further optimized with the Click&Coat system described earlier, no automatic or continuous coating techniques exist for directly coating the membrane.

In terms of new fabrication techniques, which are particularly suitable for fabricating CCMs, development is therefore focusing on coating both sides on a small scale using slot nozzles, screen printing, and ink-jet coating. The size of the system was chosen so that it allowed single sample pieces to be fabricated on a laboratory scale, and using the same process, electrodes for a complete stack (with the exception of the ink-jet). The processes listed were chosen because they complement each other well and have significant advantages over the standard coatings that can be applied using the line coater.

Fig. 19: Base coater (left), detail of the system for coating both sides (right)

A base coater (Fig. 19, left) with a coating width of 20 cm will be used for the direct coating of membranes and the coating of transfer foils using slot coating. Two different material pathways through the machine can be realized: On one pathway, one side is coated in a perpendicular position with subsequent horizontal drying. The other is a vertical pathway, where both sides are coated using slot coating followed by vertical drying (Fig. 19, right).

A screen printer is particularly suitable for the precision coating of defined surfaces. As a number of layers must be printed on top of each other in order to deposit the quantity of catalyst required for the DMFC, a DEK Horizon 03i screen printer with fully automatic alignment was purchased (Fig. 20, left). By using differently designed screens, it is possible to fabricate graded electrodes, which for example exhibit a higher catalyst loading in particularly critical areas, while the expensive catalyst can be saved in uncritical areas. In comparison to the above-mentioned techniques, screen printing is an intermittent process, which builds up the catalyst layer from a number of sublayers. This means that the fabrication of small quantities of samples for the further development of electrodes and for the optimization of the fabrication technique is particularly easy. At the same time, the feasible cycle numbers of a few hundred pieces per hour basically ensure that the technique can be scaled to an order of magnitude that is relevant for production. A drying system connected to the screen printer allows the reproducible evaporation of the dispersant and thus a uniform coat formation on the fabricated electrode.

The screen printer makes it possible to apply the catalyst layer on a gas diffusion layer as well as directly onto a membrane (Fig. 20, left). As a result, this technique is also particularly advantageous for fabricating CCMs from new membranes for testing them without running into problems caused by poor contact between an existing GDE and a new membrane, which often lead to inaccurate measurements. The reproducible fabrication of CCMs is also essential for comparing different gas diffusion media.

Fig. 20: Screen printer (left) and applying a catalyst layer (right)

1.3.2.2 Fabrication technology for stack assembly

Within the framework of activities aiming to set up a pilot fabrication facility, existing competencies were expanded and new fabrication devices and measuring systems were purchased for quality assurance.

Expanding the functionality of existing robot systems

Expanding the functionality of the existing robot made it necessary to adapt the robot's interface. A quick release system allows different tools to be connected to the robot with a change-over time of only a few seconds, whereby the robot grips the required tool itself. At the same time, the construction of the gripper has been simplified. Different grippers can now be designed for different tasks, which means that one gripper no longer has to handle all components. This also has a positive effect on reliability. The tool changing system can be used, for example, to preassemble the stack components. This involves using the robot to connect three components of the bipolar unit together. In order to do so, it is necessary to alternate between gripper and the adhesive application to stack the components and simultaneously bond them together.

The functionality of the existing robot system has therefore been expanded to include a dual-component dispensing system consisting of a dispensing unit with integrated mixing chamber und suitable materials-handling technology for highly viscous sealants in order to apply sealing components to complex geometries (Fig. 21). The control system for the dispensing technology was developed, programmed, constructed and finally connected to the robot control system based on the requirements of IEF-3. The process control system, in other words the interaction between the robot control system and the dispensing system, plays an important role in ensuring that the high quality demands are met by the sealing elements in fuel cells. Studies will be conducted in future using different sealants and sealing geometries in order to further develop the sealing process for fuel cell stacks.

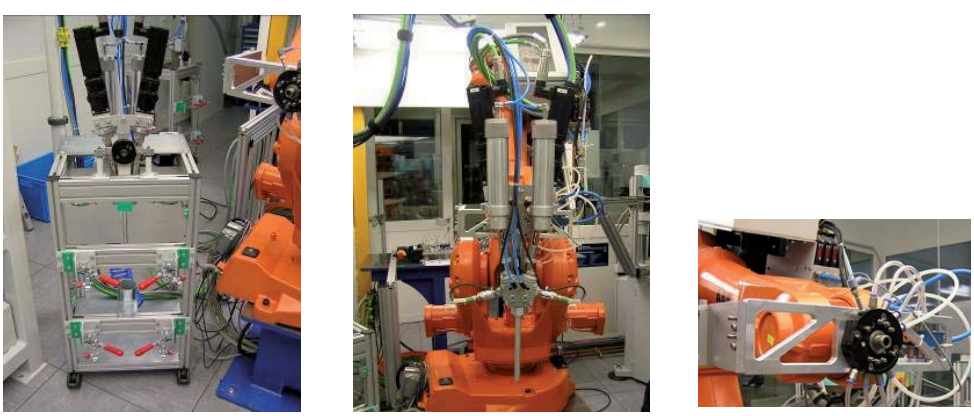


Fig. 21: Dual-component dispensing system and gripper system

Fabrication of stack components

In order to be able to use the cost-effective stamping technique in future to fabricate stack components such as sealant and flow distribution structures, a four-column laboratory press with a maximum force of 2000 kN was constructed and connected to the robot system. This makes it possible to use stamping technology, for example, to fabricate components with very long cutting edges, such as complex flow fields. Mechanically more stable materials can also be used (greater density and thickness). The ejectors in the stamping tool, however,

have proven to be in need of optimization, particularly for highly complex flow fields. They will be improved within the framework of other projects (Fig. 22).

In addition to forming processes, the fabrication of cell and stack components using metallic materials involves, for example, the coating of components in order to reduce contact resistances, and thus performance losses. The material-saving surface coating of bi-polar plates and contact plates by means of a laser coating unit can make a significant contribution to lowering the costs associated with the fabrication of fuel cell systems. Within the scope of a completed BMBF collaborative project (reference no. 01RI05084), the functionality of laser coatings was tested in comparison to flat coating, and it was shown that less noble metal was required.

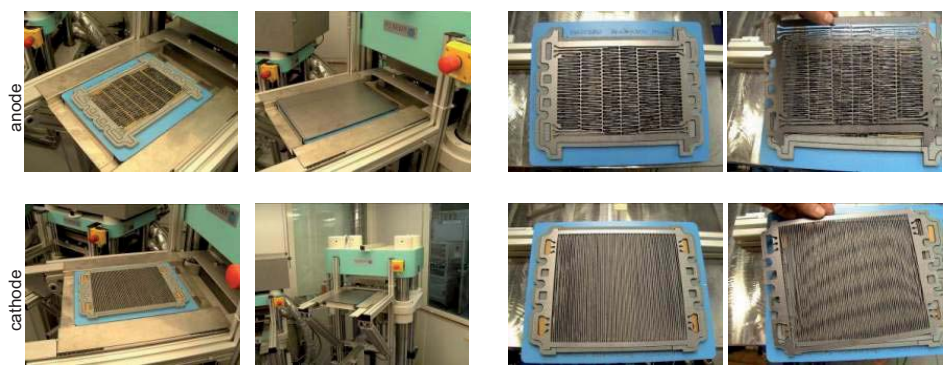


Fig. 22: Stamping of fuel cell components

In addition to coating metallic bipolar plates, there is a wealth of other applications for laser technology in a variety of fabrication steps for stack components. For example, using laser technology, it is possible to alter the surface morphology in a specific manner (for example, roughening or polishing), in order to adapt the mechanics of the plates to meet the requirements in the stack. A conceivable option, for example, would be pretreating the bipolar plate components in order to improve adhesion as part of the preassembling step.

In order to exploit the potential offered by laser technology for the fabrication of stack components, a laser machining system was constructed. The system is composed of four subcomponents, which can be operated via a central controlling unit. In the system, components measuring up to 300 x 400 mm² can be clamped and machined with a high precision (+/- 0.01 mm). The laser coating system (Fig. 23) comprises the following components:

- coating system with fixing unit and laser shielding
- laser with maximum laser power of 100 watts
- powder feeder, which transports a mixture of metal powder and carrier gas to the coating head, and
- suction unit, which removes the laser gases and dust residue from the machine.

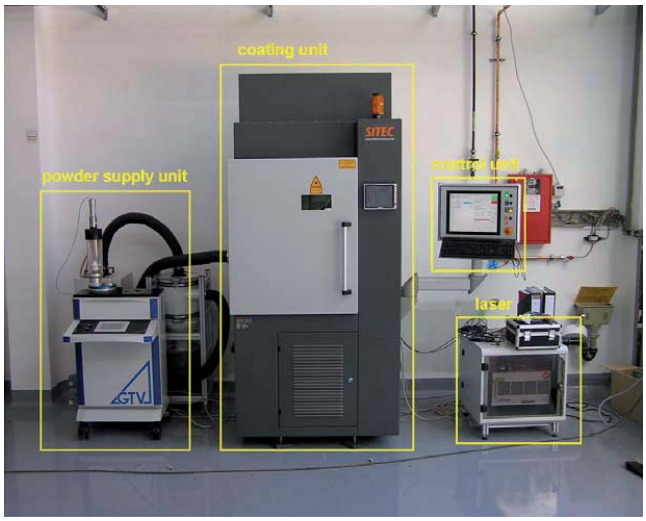


Fig. 23: Laser coating unit with subcomponents

In the coating mode, the laser beam is conducted through an optical wave guide to the coating head, where laser optics are used to focus the laser on the welding point. A mixture of metal powder and inert gas is fed into the coating head through a tube. This mixture is fed into a nozzle, which is then focused with the aid of an opening on two concentric cones. In the powder focus, the laser is used to help melt the substrate and the powder. When they cool down, an extremely stable joint is created between the coating material and the substrate. The powder/gas mixture is created with the aid of a powder feeder. In addition to argon and nitrogen, helium was proven to be particularly advantageous as a carrier gas for transporting a gold powder.

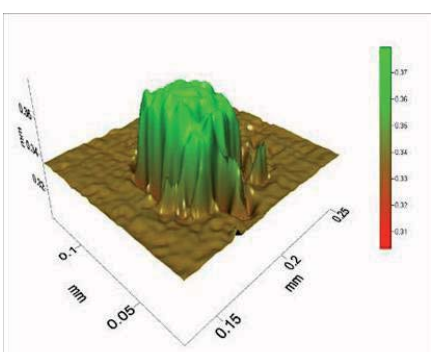


Fig. 24: Laser scan of a gold point on a nickel-based alloy

Fig. 24 shows a laser scan image of a gold dot applied to a nickel-based alloy using the coating process. The aim is to apply the technology described here for the cost-effective selective coating of bipolar plates with gold or other metals in order to reduce contact resistances. In doing so, only the functional surfaces are coated. The rest of the bipolar plate remains untreated.

In addition to the coating technique outlined above, it is also possible to equip the system with a cutting head, which allows the outer contours of bipolar plates to be processed. This makes it possible to adapt the outer contours of bipolar plates to suit the requirements in a cell stack without great expenditure or effort. Apart from the forming processes based on stamping, a complete bipolar plate can be fabricated using this system.

Quality assurance

When fabricating cell components, manufacturing tolerances must be reduced, in order to obtain fuel cell components, which will operate efficiently over a long period of time. It is essential that dimensional compliance is verified in order to reveal possible errors as early as possible. In contrast to standard components, which have a limited number of characteristic dimensions, a topographic profile of large surfaces must be created for fuel cells. This holds for components of the bipolar unit as well as for MEAs and electrodes.

Fig. 25: Non-contact 3D laser measurement system

With the aid of a non-contact 3D laser measurement system (Fig. 25) and the corresponding analysis software, measurements can be taken of contours, coating thicknesses and surfaces. These measurements are precise enough to evaluate the quality of the fabrication process (see also example in Fig. 24). An important characteristic of the system is the option of automatically scanning components with dimensions of up to 300 x 300 mm². Depending on the add-on unit, measurement accuracies of between 0.01 µm and 0.1 µm can be achieved. Such accuracies are necessary to optimize material processing. The large operating range allows cell components such as bipolar plates, end plates and MEAs to be measured in full in one run, and thus also allows their shape and storage tolerance to be tested.

When assembling a cell stack, it is vital that all cells are aligned exactly to each other. If this is not done, the flow through the channels may be impeded. For manual stack assembly, the cells are mounted using alignment pins and are continuously subjected to control checks by the assembly personnel. In order to assemble a stack with 100 cells, around 400 components are stacked on top of each other. This work demands a high level of concentration and small mistakes cannot always be avoided for such a large number of components.

Although the precision of stack assembly can be improved by using robot technology, it is still necessary to check the accuracy of positioning during assembly. This can be performed by means of a camera system installed on a robot. With the aid of such a system, the assembly of stacks can be reliably documented and the dimensional compliance can be improved. Components that have been inadequately stamped or components with deformations can thus be identified and the robot can subsequently reject them. This ensures that the functioning of the in-built flow distributors in the stack is not negatively influenced.

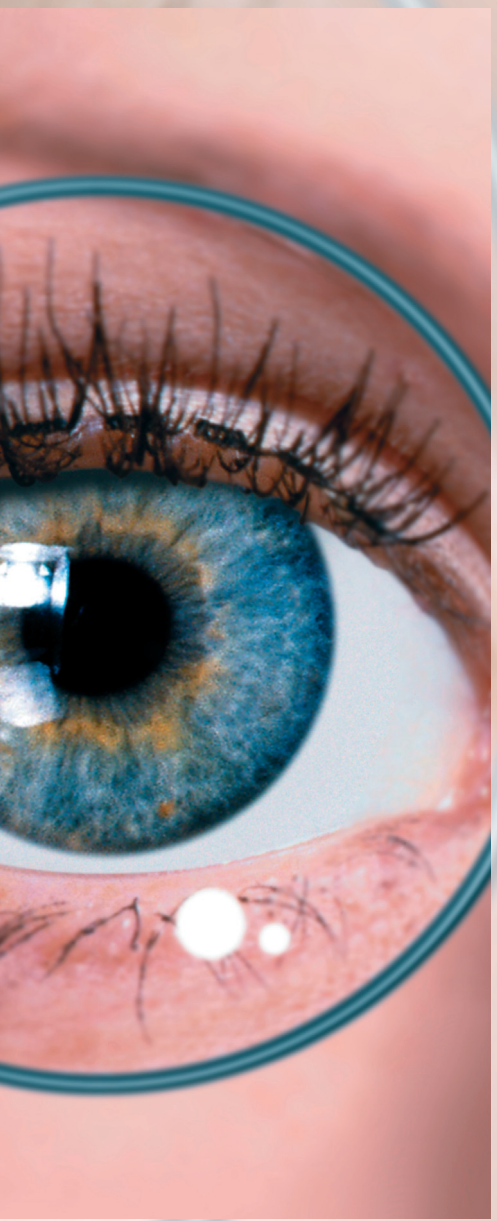
The fabrication of fuel cells and of their components can be broken down into a number of fabrication steps. The monitoring and verification of the material flows and the associated documentation are crucial processes in all fabrication steps. This is why the advanced image

processing system is also used to read barcodes. A second camera has been integrated into the fabrication process for this purpose. It has a resolution that is capable of recognizing 2D matrix codes. With the aid of this system, stack assembly in the future will be reliably and automatically documented.

1.3.3 Outlook

The research and fabrication facility for cell and stack components means that not only are classical coating techniques available, but so are new methods that allow new techniques to be developed for the fabrication of MEAs with improved structure and performance for different types of fuel cells including PEFC, DMFC and HT-PEFC. Techniques that can be used as tools for basic investigations, such as the reduction of noble metal, are also available. They make it possible to build up selected structures of electrodes and catalyst layers, which are impossible to achieve using classical coating techniques.

With the new pilot facility, the Institute of Energy Research – Fuel Cells (IEF-3) will be able to continue to participate in R&D projects aiming to produce electrodes measuring a few square meters of a consistent and reproducible quality for stack and system development in the kW class. Some of the systems available in the coating facility will, for example, be used in the near future to fabricate novel MEAs within the framework of a planned development project with an industrial development partner. The facilities can also be used by development partners for test purposes.



2

Education

Education and Training

- University education
- Further education and information events
- Training documentation
- Training facilities

Within the framework of a project funded by the Federal Ministry of Economics and the NRW Ministry of Economics (“Fuel Cell Training and Demonstration Centre”), the Jülich Institute of Energy Research – Fuel Cells (IEF-3) supported by Aachen University of Applied Sciences, Division Jülich, the University of Dortmund and bfe Oldenburg pursued a number of activities. Between 2002 and 2004, comprehensive training documents and a multimedia learning program (“Fuel Cells”, VOGEL Buchverlag ISBN 3-8023-1991-5) were finalized, training equipment was constructed and put into operation, and a wide range of information events and further training courses were held for different target groups. All measures aimed to satisfy those interested from the fields of education and training, skilled trades and industry. With the conclusion of project activities in 2004, a reorientation was undertaken in cooperation with the project partners (Fuel Cell Education and Training Centre Ulm (registered association), FhG-ISI, the Heinz Piest Institute at the University of Hannover, and Ludwig-Bölkow-Systemtechnik). This led to IEF-3 focusing on “education” as its principal task. This is the background behind Jülich’s current further education and training activities and the courses offered on the topic of “Fuel cells and hydrogen”.

2.1 University education

In line with the IEF-3 model, scientists at the institute also teach at universities in parallel to their research and development work. Within the framework of the Jülich model, IEF-3 also participates in a joint appointment process for professors with RWTH Aachen University, whereby Prof. Dr.-Ing. Detlef Stolten was appointed chair. Two chairs were also taken at Aachen University of Applied Sciences, Division Jülich, by Prof. Dipl.-Ing. Ludger Blum and Prof. Dr.-Ing. Ralf Peters. Furthermore, PD Dr. rer. nat. Werner Lehnert lectured as “Privatdozent” at the University of Ulm. Two other teaching positions were taken up at Aachen University of Applied Sciences, Division Jülich, by Dr.-Ing. Bernd Emonts and Dipl.-Ing., Dipl.-Wirt.Ing. Thomas Grube.

Fig. 26 : Universities where IEF-3 staff lecture

The spectrum of topics taught range from the basics of science and theoretical modeling and simulation methods to detailed technical knowledge and the characterization of technical applications. In total, seven lectures and three seminars are taught each semester in the form of double lessons. Moreover, a half-day practical course is offered every summer semester. The number of students participating in the individual courses each semester varies between ten and fifty. The scientists at IEF-3 also play an important role supervising term papers, diploma dissertations and PhD theses. In 2007, nine diploma and master

dissertations and two PhD theses were successfully submitted, while in 2008 eleven diploma and master dissertations and two PhD theses were completed.

2.1.1 Courses taught by professors

Tab. 1 provides an overview of the courses taught at universities by the professors at IEF-3.

Name	Topic	Type/hours Semester		University
Prof. L. Blum	Brennstoffzellen – Die Zukunft der dezentralen Energieversorgung!?	V/2	WS	Aachen Univ. of Applied Sciences, Division Jülich
	Fuel Cells – The Future for Dispersed Power Supply!?	V/2	SS	
Prof. Dr. R. Peters	Basics and applications of chemical reaction theory – simulation of dynamic processes in energy systems with MATLAB/Simulink	V/2 S/2	WS	Aachen Univ. of Applied Sciences, Division Jülich
Prof. Dr. D. Stolten	The basic principles and technology of fuel cells	V/2 S/2	WS	RWTH Aachen University

Tab. 1: Courses taught by professors

2.1.1.1 Fuel cells – The future for dispersed power supply!?

Prof. Ludger Blum teaches the specialist subject of fuel cell technology at Aachen University of Applied Sciences, Division Jülich. The optional subject “Fuel cells for stationary applications” in the undergraduate course on energy and environmental technology and the masters course on energy systems covers the function, construction, behavior, and advantages and disadvantages of different types of fuel cells. It also lays the groundwork for the process engineering design of fuel cell systems. The topics include: basic principles of fuel cells; fuel supply; efficiency, function and construction of different types of fuel cells; fuel cell system requirements; process engineering of various fuel cell systems for different applications; energy balance of a fuel cell system; and modern plant engineering. An average of twelve students took the course each semester.

2.1.1.2 Basics and applications of chemical reaction theory – simulation of dynamic processes in energy systems with MATLAB/Simulink

Prof. Dr.-Ing. Ralf Peters is responsible for teaching energy process engineering at Aachen University of Applied Sciences, Division Jülich. The course “Basics and applications of chemical reaction theory – Simulation of dynamic processes in energy systems with Matlab/Simulink” links the basic principles of chemical process engineering with dynamic

simulations of reactors. The lectures and seminars use the following as examples: fuel processing and fuel cell system technology for methanol fuel cell drive systems and for diesel-based on-board power supply. The course is compulsory for the 30 – 40 students enrolled in the Master of Science in Energy Systems.

2.1.1.3 The basic principles and technology of fuel cells

Prof. Dr.-Ing. Detlef Stolten holds the chair for fuel cells at RWTH Aachen University. The courses offered focus on converting renewable and fossil energy carriers for use in fuel cells for portable, stationary and mobile applications. The process engineering and systems technology aspects cover high-temperature and low-temperature fuel cells, as well as the processing of fuel for fuel cells. These elements are accompanied by an examination of the basic physical and chemical principles involved. Systems analysis studies on energy process engineering, including how to estimate costs, round off the coverage of the subject with a view to future market launch. During the 2007/2008 winter semester just under 50 students attended the lectures and seminars. As part of the existing cooperation with Forschungszentrum Jülich, the chair offers students the chance to work on term papers and diploma dissertations and also provides them with an opportunity to work on projects as research assistants.

2.1.2 Courses taught by university lecturers

Tab. 2 provides an overview of the courses taught at universities by members of staff at IEF-3.

Name	Topic	Type/hours Semsester		University
Dr. B. Emonts	Hydrogen and ist conversion via electrolysis and the fuel cell process	L/2	WS	Aachen Univ. of Applied Sciences, Division Jülich
	Elektrolyzers and fuel cellse	P/4	SS	
Th. Grube	Basics and Applications of Chemical Reaction Theory – Simulation of Dynamic Processes in Energy Systems with Matlab/Simulink	S/2	WS	Aachen Univ. of Applied Sciences, Division Jülich
PD Dr. W. Lehnert	Fuel Cells – From the basics to applications	L/2	SS	University of Ulm
	Eletrochemical process engineering	L/2	WS	

Tab. 2: Courses taught by university lecturers

2.1.2.1 Hydrogen and its conversion via electrolysis and the fuel cell process

Dr.-Ing. Bernd Emonts lectures at Aachen University of Applied Sciences, Division Jülich, on the subject of electrolyzers and fuel cells and holds a four-hour practical course for small groups (5 – 10 students). The course of lectures provides an introduction to the basic electrochemical principles of both conversion processes, explains the design of different types of devices, and presents examples of proven applications. The subsequent practical course is carried out under supervision at IEF-3 on an energy storage system with a pressure electrolyzer and PE fuel cells, as well as pressure storage tanks for hydrogen and oxygen. The main operating parameters are recorded by the students, who then determine the operating characteristics and the device efficiency.

2.1.2.2 Fuel cells – From the basics to applications

Dr. Werner Lehnert ("Privatdozent") lectures at the University of Ulm. His lecture "Fuel cells – From the basics to applications" is part of the interdisciplinary course on energy technologies for students enrolled in science and engineering. It takes place during the summer semester. The course provides an introduction to the different fuel cell technologies before looking at the electrochemical, chemical and physical principles. One of the main emphases is a description of modern methods of investigation, such as synchrotron and neutron radiography and tomography, which are used to noninvasively image liquid water in situ in cells and stacks. Technologies that produce hydrogen, entire fuel cell systems and their application are also taken into consideration. An average of 30 students attend the lectures.

2.1.2.3 Electrochemical process engineering

PD Dr. Werner Lehnert targets chemists in the final years of their studies with his lectures on "Electrochemical process engineering" at the University of Ulm. The lectures are held during winter semester and are attended by between six and ten students. The main issues addressed are the fields of mass and heat transport processes in electrochemical process engineering and the energy balance of reactors. Different types of electrochemical reactors and their application in an industrial setting are also dealt with.

2.2 Further education and information events

The range of events organized for further education and the provision of information is just as diverse as the needs of the groups themselves. In order to adequately meet the demands made on a particular research institute for training and information, a variety of different events are organized by IEF-3. IEF-3 is also involved in external events on various levels and works with other institutions preparing, coordinating and offering advice.

2.2.1 Organization of seminars, practical courses, information events and visits to the institute

The topics dealt with at the events depend on the requirements and requests of each target group. This means that the events range from information events and training courses for secondary-school students, university students, teachers, tradesmen, technicians, engineers and scientists to practical courses on career choice and work experience for secondary-school students, as well as vocational training and study-related placements for third-level students. The length of each of the events ranges from a half day to a number of weeks depending on the situation. The tasks assigned to secondary-school students and university students during a placement range from shadowing technical and scientific staff at the institute to supervised independent work on selected practical projects.

- Vocational training and work experience for secondary-school students from local schools on the topic of “Specialist careers in fuel cell technology” (2007: 12 students and 2008: 15 students on placement)
- Seminar for secondary-school students and teachers (2007: 13 people) at the ProMiNat academy on the topic of “Energy from fuel cells” as part of their Jülich research placement
- Seminar for secondary-school students and teachers (2007: 40 people and 2008: 25 people) from the Immanuel Kant Grammar School, Dortmund, on the topic of “Fuel cell systems and hydrogen”
- Information events and visits to the institute for those interested (2007: 60 events with approx. 1,200 participants and 2008: 82 events with a total of more than 1,400 participants) on the topic of “Fuel cell technology”
- Development of an interactive presentation entitled “Fuel cell research in Jülich” and its presentation at national and international exhibitions and trade fairs (2007: 4 exhibitions/trade fairs and 2008: 7 exhibitions/trade fairs)
- Presentation of the R&D topic of “Fuel cell technology” at the Jülich partner day “Research and SMEs”
- Presentation of the R&D topic “Fuel cell technology” at the Central Library’s conference “Scholarly Communication of the Future” at Forschungszentrum Jülich
- Participation in the development and implementation of a “hydrogen and fuel cells” schools laboratory as the first of its kind in the Jülich Schools Laboratory with seven one-day practical courses, in which a total of 150 senior students from secondary schools participated

2.2.2 Involvement in external events

Members of staff from IEF-3 were invited to speak at several external events, where they gave general introductions to “fuel cell technology” or presentations on selected specialized fields within the subject. The first day of the 4th German Hydrogen Congress 2008 (Fig. 27) in Essen is a good example of the range of topics that can be covered in an educational information day for secondary school students, university students and teachers. The day-long event provided the some 150 participants with the most important information regarding the basic scientific and technical features and application-oriented systems, as well as an overview of the available opportunities for qualification and job descriptions relevant to the area of “hydrogen and fuel cell”.

Fig. 27: The further education and information event in Essen in February 2008

- Workshop for developers and users of fuel cells on the topic of “Predictions on the service life of fuel cells” as part of the WBzU events in Ulm
- Specialist seminar for scientists, developers, engineers and inventors working in the field of propulsion engineering on the topic of “Small fuel cell drives” as part of the WBzU events in Ulm
- Presentation for specialists and interested individuals on the topic of “Fuel cells: Prospective fields of application in building technology – development status” within the scope of a conference organized by the NRW Professional Association for Electrical Engineering and Information Technology Trades in Dortmund
- Exhibition and provision of information on applications of fuel cell technology as part of the event organized by the German Technology Museum in Berlin entitled “Researchers experiment, explain and provide answers”
- Exhibition and provision of information on applications of fuel cell technology within the framework of “Highlights of Physics 2007”, an event organized by BMBF and the German Physics Society in Frankfurt
- Round-table discussion on the topic of “A fuel cell network for the Aachen region?” as part of a discussion forum on fuel cells in the Oberbruch industrial park
- Unveiling of an interactive presentation entitled “Fuel cell research in Jülich” at national and international exhibitions and trade fairs (2007: 4 exhibitions/trade fairs and 2008: 7 exhibitions/trade fairs)

- Educational information day for secondary-school students, university students and teachers as part of the 4th German Hydrogen Congress 2008 with approx. 150 participants
- Tutorial for young professionals and other individuals interested in the scientific and technical aspects of fuel cells as part of the Lucerne Fuel Cell Forum 2008
- NOW workshop on "Training and qualifications in the field of hydrogen and fuel cells in Germany" for representatives of associations, chambers, professional associations and industry in order to identify specific training and training measures in the National Innovation Program (NIP)

2.2.3 Collaboration with other organizations

Designing, launching and implementing further education and training measures and qualification programs on the topic of "Fuel cell technology" are increasingly becoming the focus of attention both in the manufacturing industry and the relevant educational establishments. In order to cater for this demand, special initiatives have been launched. The combination of specialist technical knowledge and existing opportunities provide an excellent basis for collaboration.

- Involvement in the Fuel Cells Qualification Initiative (IQ-BZ), working to implement information and training measures for fuel cells and hydrogen technologies
- Preparation of a project tender through the Fuel Cells Qualification Initiative (IQ-BZ) for conducting tasks on the topic of "Information and qualification" for a consortium that is preparing a comprehensive project proposal entitled "Fuel cell heating units"
- Continuation of the activities of the "Fuel Cells Training Network" consortium and continuing maintenance of the joint Internet portal
- Promotion and sale of a "Fuel Cells" CD-ROM through the Federal Technology Centre for Electrical Engineering and Information Technology, Oldenburg, and Vogel Industrie Medien GmbH, Würzburg, which is designed to provide information, increase the acceptance of fuel cells, and promote further training
- Adaptation of existing teaching modules to meet consumer demands
- Support and incorporation of training centers and centers of excellence (WBzU and RAG Bildung) in the planning and realization of joint training events held at the respective center
- Preparation, coordination and realization of an educational information day for secondary school students, university students and teachers as part of 4th German Hydrogen Congress 2008 in cooperation with the University of Duisburg, WBzU, and the EnergyAgency.NRW
- Preparation and coordination of educational and information events for secondary school students, university students, teachers and members of the public, which will take place within the framework of the 18th World Hydrogen Energy Conference 2010 in cooperation with representatives from the University of Duisburg, WBzU and the EnergyAgency.NRW
- Involvement in drawing up a project outline through the Herten technology development and investment company aiming to design a qualification measure for "hydrogen and fuel cell service engineers"

– Setting up of a working group – on 26 August 2008 in ZukunftsZentrum Herten – and involvement finalizing fuel cell/hydrogen training measures for the Recklinghausen district and the Emscher-Lippe region drawn up by the Herten technology development and investment company and RAG-Bildung

Schools Laboratory

The Jülich Schools Laboratory has set itself the task of introducing students to the world of science, including hydrogen and fuel cells, by encouraging them to conduct their own experiments. Five experiments have been developed for this purpose, and students perform them in order to find theoretical and practical solutions to the following:

- generation of hydrogen from water
- construction of a low-cost fuel cell
- characterization of a fuel cell
- determination of the efficiency of an electrolyzer and a fuel cell

Experiments are conducted under supervision in the well-equipped Schools Laboratory (Fig. 28). Students must be familiar with how to conduct experiments from chemistry and physics classes. For this reason, they are performed with senior secondary-school students. Approximately three double classes are required to complete the experiments.

Fig. 28: Students conduct experiments in the Schools Laboratory on the topics of "hydrogen" and "fuel cells"

2.3 Training documentation

Based on project activities over a period of three years and involvement in the third-level sector through presentations in universities coupled with participation in scientific and technical conferences, IEF-3 is in a position to provide comprehensive training material that reflects the current state of research, development, demonstration and application. This includes the multimedia learning program “Fuel Cells” published by VOGEL Buchverlag (ISBN 3-8023-1991-5) as well as a number of PowerPoint presentations on specific topics. Existing operating, maintenance and troubleshooting guidelines are based on test devices for fuel cells and system components which were dismantled during the course of renovation and expansion measures. Descriptions of the construction, application and evaluation of tests and experiments on water splitting using electrolysis and on hydrogen conversion using fuel cells come from the Jülich schools laboratory. Their primary aim is to encourage students to perform their own experiments in an independent manner.

2.4 Training facilities

At the moment, IEF-3 has access to the two industrially relevant experimental modules shown in Fig. 29 for activities with participants of training events. One system has a modular design and is based on direct-methanol fuel cells (DMFCs). It has an electric power of 2 kW and is particularly suitable for demonstrating how individual hardware and system components function, how they are dismantled and how they are assembled. Trainees gain specialist knowledge and practical experience dealing with fittings and devices from the fields of mechanical engineering, process engineering, energy systems, heat transmission technology and electrical engineering, as well as chemistry and physics.

The operational energy storage module has an alkaline pressure electrolyzer (AEL: 1 kW @ 30 bar), a polymer-electrolyte fuel cell (PEFC: 0.5 kW), and storage tanks for hydrogen and oxygen (H_2: 10 l @ O_2: 5 l) including power electronics and software-programmed control mechanisms (SPS). The system allows both electrochemical converters AEL and PEFC to be characterized and the system characteristics to be studied. The energy storage function in the form of compressed hydrogen is particularly interesting here. A manuscript introduces the device functions and provides the basis for assignments aiming to determine the characteristics, energy fluxes and performance.

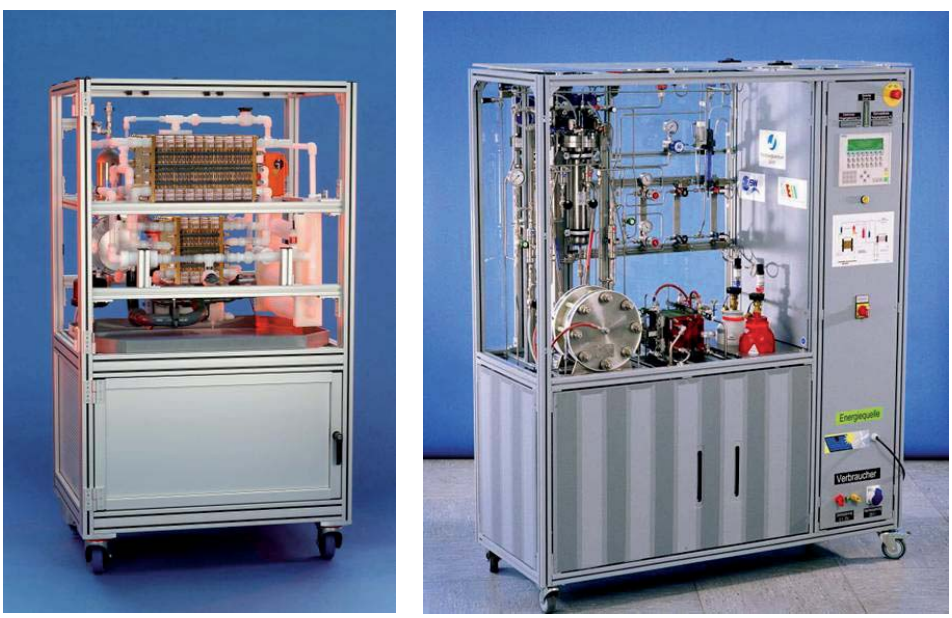
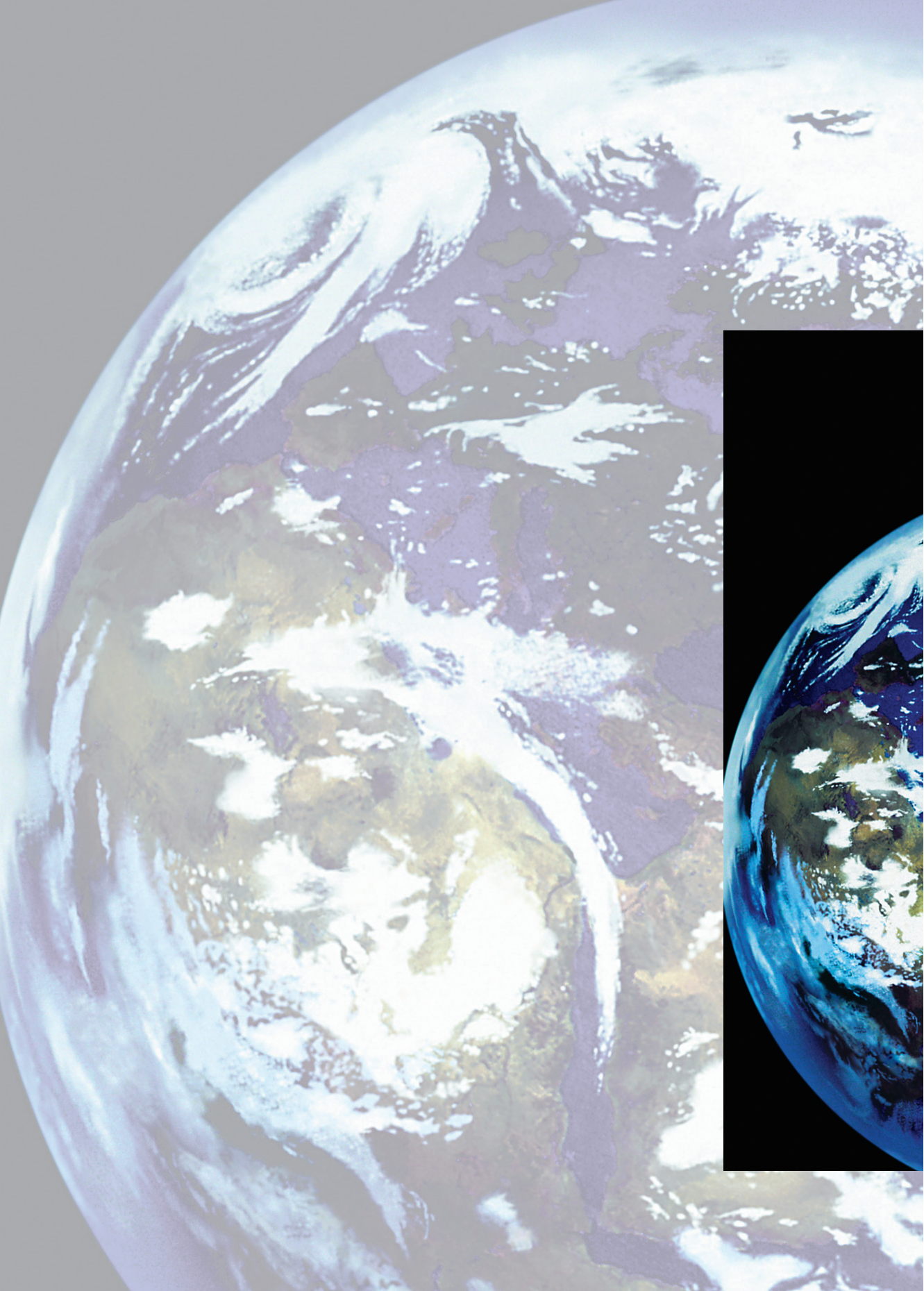
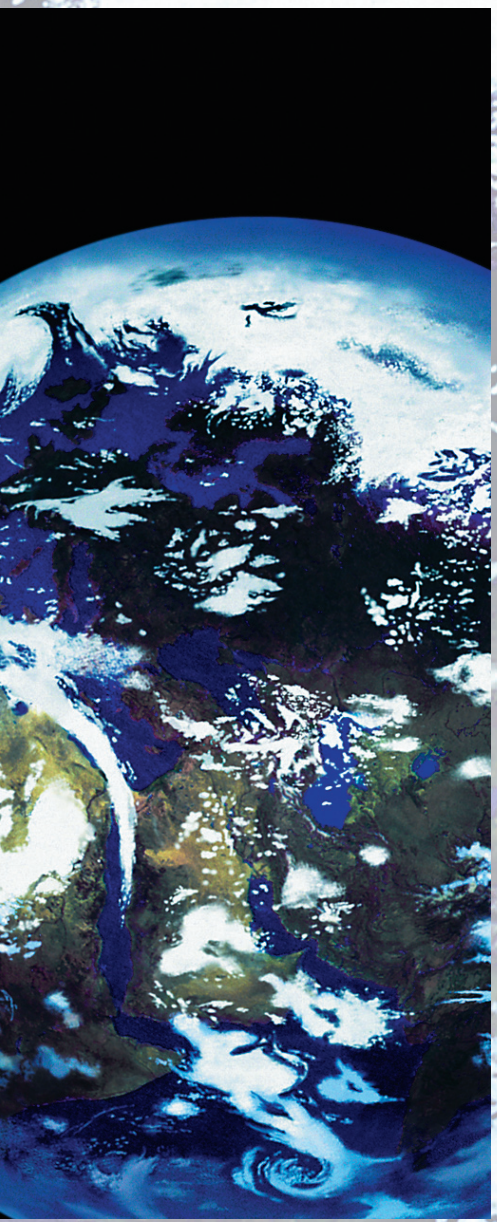


Fig. 29: Industrially-relevant experimental modules: DMFC system (left) and energy storage module (right)





3

Reports

Scientific and Technical Reports

- Key topic: direct methanol fuel cells
- Key topic: high-temperature polymer electrolyte fuel cells
- Key topic: solid oxide fuel cells
- Key topic: fuel processing systems
- Interdisciplinary topic: process and systems analysis
- Interdisciplinary topic: analysis
- Interdisciplinary topic: quality management

3.1 Key topic: direct methanol fuel cells

3.1.1 Objectives and fields of activity

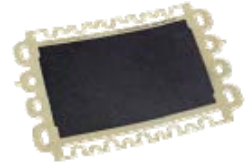
Direct methanol fuel cells (DMFCs) provide an interesting alternative in the short-to-medium term to lead-acid batteries, which are currently used for small mobile applications (e.g. in the field of material handling) thanks to their large range and the fact that they are easy to refuel. IEF-3 has therefore made the research and development of DMFC technology one of their main priorities.

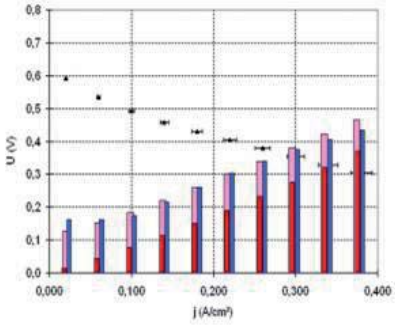
Activities focus on increasing the overall efficiency, power density, and service life of fuel cells, while simultaneously decreasing the manufacturing costs. In order to achieve these objectives, degradation mechanisms must be identified, material and manufacturing costs must be reduced for stack components and MEAs, the quality must be increased, and a highly integrated fabrication technique must be mastered. The challenge in terms of applications lies in optimally integrating fuel cells into energy (hybrid) systems and realizing a closed water circuit during system operation. Important flanking activities are pursued in the area of analysis within the framework of studies on the structure-activity relationships of functional layers and the spatially resolved electrochemical and physiochemical characterization of fuel cell components.

3.1.1.1 MEA development and fabrication

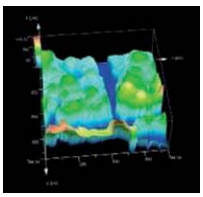
A prerequisite for launching DMFCs on the market in the area of portable and small mobile applications is not only high power density and sufficient long-term stability but also a cost level that is comparable to existing technologies. The specific electric power of the MEA directly influences the size of the fuel cell stack and thus the power density and cost of the entire system. The major cost drivers are the noble metal catalysts for electrocatalysis in the electrodes.

Work on the further development of MEA components therefore concentrates on optimizing media transport and the electrical properties in the individual functional layers in order to improve the performance and efficiency of MEAs and thus make stable DMFC operation under load a reality, even for low air flow rates (and balanced heat budget).





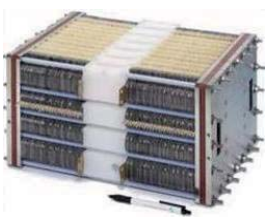
These activities are supported by electrochemical and structural studies. The electrochemical characterization of an MEA focuses particularly on analyzing the relationships between input parameters, such as operating parameters, and observed parameters, such as cell voltage, and on describing system performance. The characterization must incorporate interactions between the physicochemical processes that occur in the MEA, such as electrochemical reactions, methanol permeation and water evaporation, and it must mathematically describe relationships with the operating parameters.



Particular attention is paid to the development, configuration and application of special measuring techniques for the structural analysis of components in the MEA and for the characterization of stacks and single cells. Highest priority is given here to the clarification of degradation effects in the MEA.

In terms of the further development of manufacturing processes for MEA components, the focus is on the continuous mechanized fabrication of gas diffusion electrodes (GDEs), and more particularly, on developing suitable catalyst inks for applying the catalyst layer on diffusion layers using different coating techniques on a pilot scale.

3.1.1.2 Stack and system development



DMFC stack development is pursued at the interface between MEA development, MEA characterization and systems technology. An important field of work here is communicating and balancing the development objectives among the various spheres of work. Practical work can be broken down into the following fields: design, construction, fabrication, assembly and testing with the aim of developing high-performance DMFC stacks with long-term stability, which can be operated with low excess air.

Systems technology focuses on designing and constructing efficient fuel cell energy systems using DMFCs as a basis. This requires in-depth knowledge not only of the cell but also of the entire system, which represents a challenge for development work. Priority here is on developing new system concepts, testing and evaluating them, developing system components in cooperation with industry, and testing and developing control system concepts.

3.1.1.3 Modeling

The aim behind DMFC modeling is to gain a basic understanding of the physicochemical processes on different time and length scales, on the one hand, and to use this knowledge for the further development of DMFCs, on the other. The numerical and analytical models for cells and stacks are based on fundamental fluid dynamic laws and electrochemical laws. Modeling aims to increase our understanding of the physical processes that occur during cell and stack operation and to test optimization measures.

3.1.2 Important results

3.1.2.1 MEA development

Membrane electrode assemblies are composed of a number of layers, each of which must perform its respective task optimally. Furthermore, they must also function in interaction with

each other. The development objective is two-fold: on the one hand, a high power density must be achieved for comparably high single cell voltage, while on the other, a stable voltage level must be ensured under load, particularly for low air flow rates, in order to allow the DMFC system to be operated in a water-autonomous manner at ambient temperatures of up to 35 °C.

Gas diffusion layers

Gas diffusion layers are usually fabricated by blade coating a carbon PTFE paste on a suitable carbon substrate. The paste usually contains PTFE in order to protect the fabricated diffusion layer during operation against flooding of the pores. PTFE is particularly challenging in terms of the development and realization of stable homogeneous pastes. At the fabrication stage, the separation of PTFE and solvent must be prevented. This problem was aggravated by the fact that the manufacturer of the PTFE dispersion had to alter the preparation formula and replace the perflourinated tenside APFO, as there is ecological concern surrounding its use. The result of this was that the composition of the dispersion had to be changed. It initially proved impossible to fabricate stable, machine-processable pastes using the new dispersion. The fabrication process was subsequently thoroughly investigated. This revealed that segregation of the paste occurred when the paste heated as a result of energy transfer during stirring to a temperature higher than 30 °C. The formulation was dispersed in a container with cooling jacket at 10 °C, which meant that the energy transferred was immediately dissipated, which in turn prevented the paste from heating up. This new process stabilized the paste and the PTFE distribution was just as homogeneous as had been the case for the PTFE dispersion containing APFO.

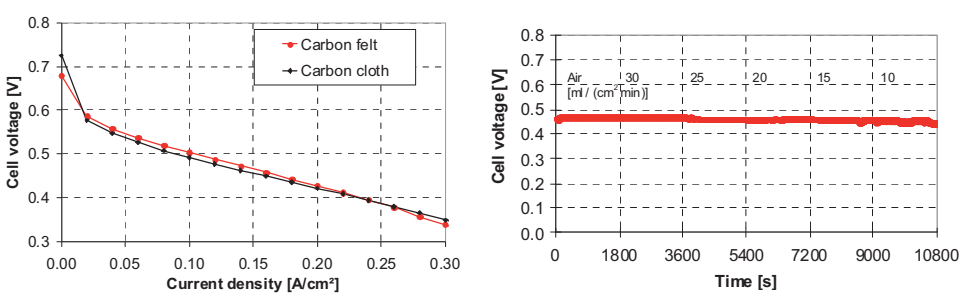


Fig. 30: **Current-voltage curves with a nonwoven substrate and woven substrate are comparable (70 °C, anode: 1 M MeOH, 0.21 ml/(cm²min), cathode: air, 37 ml/(cm²min); left), stability of cell voltage down to low air flow rates (70 °C; 0.14 A/cm², anode: 1 M MeOH, 0.21 ml/(cm²min); right)**

At the moment, carbon tissue is used as a substrate for electrodes. It has very good diffusion characteristics, but it is extremely flexible, which means that it contributes little to the mechanical stability of the MEA. This is the reason why the fabrication of gas diffusion electrodes was tested on more rigid materials, such as carbon fleece. A combination of different nonwoven materials led to the fabrication of MEAs, which exhibit a performance

comparable to the MEAs currently in use, in which carbon tissue functions as the diffusion layer, and which have a constant voltage even for low air flow (Fig. 30).

Catalysts

Carbon-supported catalysts for fuel cells were originally mainly fabricated using carbon black XC72 as a substrate. Noble metal loadings of up to 60 wt % were commercially available for this purpose. Catalysts on carbon substrates with very high specific surfaces and catalysts with a very high proportion of noble metals (up to 80 wt %) are now commercially available. These catalysts promise higher catalyst activity. As a result, a range of new catalysts were tested, retaining noble metal contents of 2 mg/cm² Pt on the cathode and 2.5 mg/cm² PtRu on the anode.

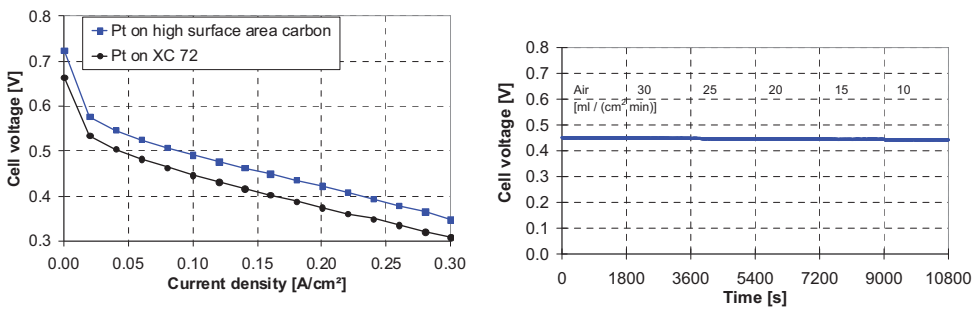


Fig. 31: Voltage increase as a result of new cathode catalysts (70 °C, anode: 1 M MeOH, 0.21 ml/cm²min, cathode: air, 37 ml/(cm²min); left), stability of cell voltage down to low air flow rates (70 °C; 0.14 A/cm², anode: 1 M MeOH, 0.21 ml/(cm²min); right)

While the new cathode catalysts led to a better performance under all conditions (Fig. 31 left), the differences between the anode catalysts were only observed under the most critical test conditions at a low air flow rate. With the best catalysts, an air flow rate down to 10 ml/(cm²min) gave rise to a stable cell voltage (Fig. 31 right). However, strong interactions occur here between the diffusion layer and the catalyst layer. The catalysts used were fabricated in IEF-3 on diffusion layers based on carbon tissue. They did not deliver optimal results on diffusion media from a third-party manufacturer. Better results were achieved by choosing another type of catalyst. The selection of high-performance catalysts now available makes it possible to select the most suitable type of catalyst for different diffusion media. In endurance tests of up to 1,000 hours, no differences were found between the catalysts tested. The highest-performing and most reliable catalysts were therefore used.

Electrochemical MEA characterization

The basic aim of the characterization of an MEA is to analyze the relationships between input parameters, such as operating parameters, and observed parameters, such as cell voltage, and to describe the system performance. If the system has to deal with constraints when it is being operated, for example, if a certain efficiency is required, this tends to have a huge influence on how the system is operated.

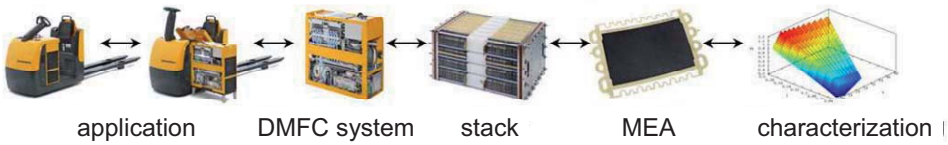


Fig. 32: From application to MEA characterization. A comprehensive analysis is important for electrochemical characterization

Intensive cooperation between MEA characterization and stack and system development led to the recognition that many of the results of previous characterization measurements for each respective application could not be assumed to be correct because the MEAs investigated behaved differently under the conditions in an application system than under the conditions that are usually set in a test system for characterization. For the application of DMFC systems in forklift trucks, a procedure was therefore derived from the specifications of the forklift, which can be used from now on to test how suitable MEAs are for use in such systems and to calculate the required system management for test systems. Only by operating the system in this specific way can the measured data from the test system be compared with those of the subsequent application system.

The decisive factor in development was that the complete chain from the forklift and the DMFC system to the stack and MEAs be considered, and that an MEA characterization procedure be developed from the respective specifications (Fig. 32).

The biggest incentive for retrofitting a battery-operated forklift truck with a DMFC operating system is the relationship between short charging times, in other words filling it up with methanol, and long operating times, which depend mainly on the size of the tank and the efficiency of the system. The DMFC has clear advantages over the lead-acid battery in this respect. In order to allow the benefits of these advantages to be felt, the application must be run on pure methanol and not on a methanol-water mixture. The water required for internal circulation must therefore be recovered from the exhaust air so that only the reaction water is allowed to leave the application. This requirement demands a time-resolved water balancing for characterization. In order to extend the operating time of the application, the application must convert the chemical energy in methanol into electrical energy as efficiently as possible. Tests therefore require additional time-resolved processes in order to quantify electrochemical methanol conversion and the loss processes.

The above considerations mean that the characterization must be able to clarify and mathematically describe the interaction between the physicochemical processes that occur in the MEA. In doing so, electrochemical reactions, methanol permeation and water evaporation must be investigated simultaneously in suitable test cells in relation to different operating parameters. This is possible using the procedure developed in IEF-3. Moreover, it was revealed that in previous measurements, such as the U(j) characteristics, the aforementioned processes were not in thermal equilibrium. However, this is an important prerequisite for subsequent operation in a DMFC system, where no heat is available.

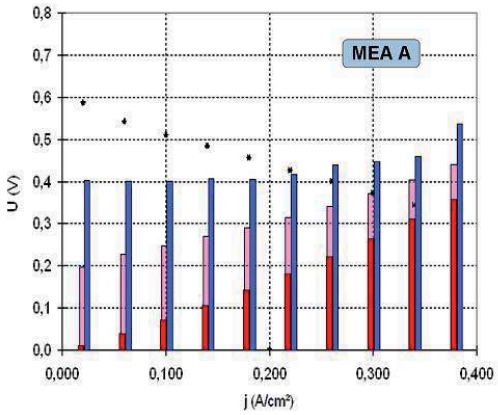


Fig. 33: The U(j) characteristics measured in a test rig with uncoupled operating parameters. The red (pink) bars represent the strength of the heat source of the electrochemical reaction (methanol permeation) and the blue bars the strength of the heat sink caused by water evaporation in the MEA

Fig. 33 clearly shows that the heat sources (red and pink bars) are not in equilibrium with the heat sinks (blue bars). In a test system, the difference is usually compensated by a heating unit. This leads to a situation where the MEA conditions investigated are only possible if a heating unit is used. In DMFC system operation, these conditions cannot be adjusted and are therefore irrelevant.

The characterization technique developed makes use of novel measurement protocols to determine the necessary information by coupling the operating parameters as required, thus allowing the identification of conditions that are stable without heating. As shown in Fig. 34, the heat contributions made by the processes described earlier can thus be brought into equilibrium with each other. This allows those MEA conditions that are relevant for application in a DMFC system to be investigated.

In the period under review, the new characterization technique was developed, and a dedicated measurement area with the required test facilities was set up and put into operation. Since the middle of 2008, this technique has been used for series measurements in connection with MEA development.

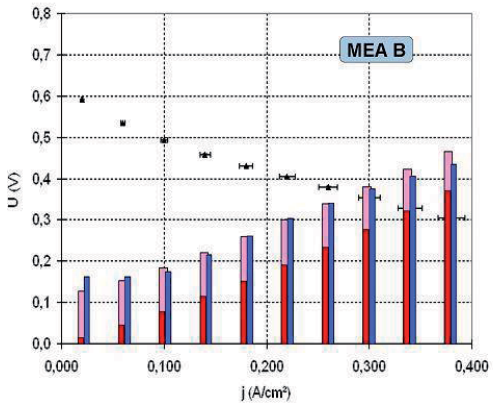


Fig. 34: **The U(j) characteristics measured in a test rig with coupled operating parameters. The red (pink) bars represent the strength of the heat source of the electrochemical reaction (methanol permeation) and the blue bars the strength of the heat sink caused by water evaporation in the MEA**

In addition to further developing existing characterization techniques with the stack and system developers, the procedure consisting of MEA fabrication, sampling, documentation, and characterization was standardized and accelerated in combination with MEA development. These were the prerequisites for a significant increase in the reproducibility and therefore in the reliability of the measurement results. In 2005, it was not unknown for comparable MEAs to deliver very different results in different test rigs (Fig. 35). Today, however, increased reproducibility makes it possible to use completely new tools.

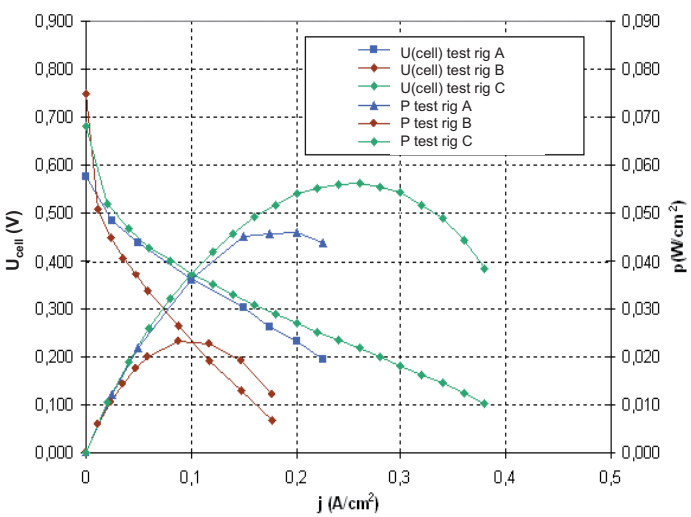


Fig. 35: **Results from 2005: some of the specimens produced in a comparable manner delivered different results in different test rigs**

For example, it is now possible to run statistical tests because a large number of specimens can be analyzed repeatedly in a relatively short timeframe (Fig. 36). Using this technique, for example, we can determine whether the measurement results are normally distributed or not. This is particularly significant for uncertainty considerations of the results of more extensive calculations based on measurement results.

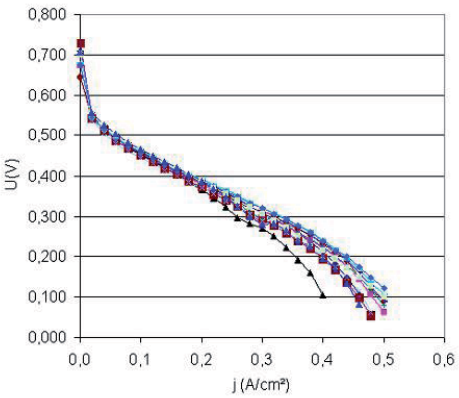


Fig. 36: **U(j) characteristics of 27 specimens, each of which was analyzed three times. The statistical distribution can now be investigated in the working range from 50 mA/cm² to 250 mA/cm²**

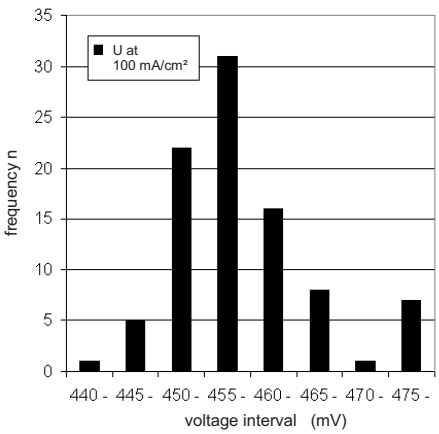


Fig. 37: **Graph of the frequency distribution of the voltage values of the 27 MEAs investigated**

The frequency distributions (Fig. 37) can now be analyzed and used to reveal the influence of effects in MEA fabrication or other areas. If all processes function as expected, the result should be a Gaussian distribution.

Degradation studies

Degradation experiments focused on systematically investigating selected aged stack MEAs from the electric vehicle JuMOVe 2, which was equipped with a DMFC system in 2007 (see IEF-3 Report 2007), in comparison to unaged MEAs, and on systematically investigating the drop in performance when turned off.

Post-mortem analysis of stack MEAs: After being dismantled, the stack MEAs displayed visually recognizable changes in all components which occurred during scooter operation. These anomalies were analyzed using X-ray fluorescence analysis (XRF) in the Central Division of Analytical Chemistry (ZCH). The qualitative results are summarized in Fig. 38. The copper contacts in the single cells were identified as the cause of the deposits containing copper. These contacts have since been replaced by stainless steel. Aluminium, silicon and phosphorus were found both in the cathode frame as well as in the Sigraflex bipolar plates. The frame material and the Sigraflex bipolar plates also contained iron and chloride. Although the various materials had already been pretreated, contaminants such as heavy metals and complexing agents (especially chloride) still managed to enter into the

stack MEAs. The pretreatment methods will therefore have to be further improved and materials may have to be replaced.

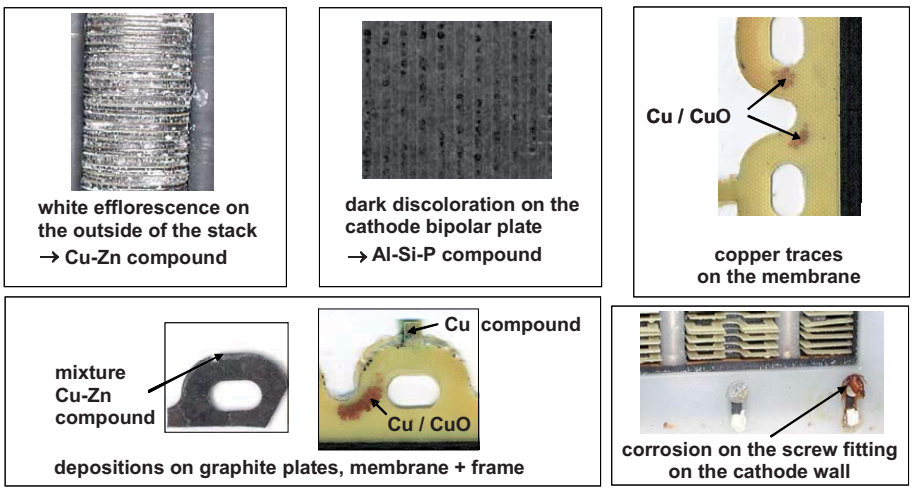


Fig. 38: Results of the XRF investigation of MEA and stack components after scooter operation in JuMOVe 2

Due to inhomogeneous operating conditions, such as nonuniform distribution of the media over the electrode surfaces, the local current density, local overvoltage and thus the local degradation of a scooter MEA are position-dependent. This was verified by cutting selected scooter MEAs into six pieces each, and turning them into small MEAs, each with an active area of 18 cm².

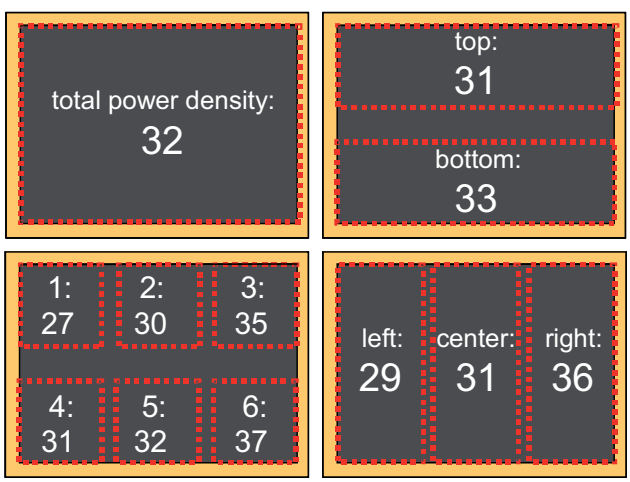


Fig. 39: Averages of the power in mW/cm² of seven aged scooter MEAs from the JuMOVe 2 stack, viewed from the anodes

The electrochemical characterization of these sections revealed that the average power of the scooter MEAs after an operating period of 500 hours was just roughly 32 mW/cm², in

other words, one third of the original value (see total power in Fig. 39). As Fig. 39 shows, the power distribution across the surface of the scooter MEAs is indeed inhomogeneous. Seen from the anode side, the power rises distinctly from left to right, whereas in the lower part of the scooter MEAs (air inlet, methanol outlet) the power is slightly higher.

Since the corroded copper tags are located in the left-hand part of the MEA, poisoning of the catalyst with copper could be responsible for the lower power in the left-hand area of the MEA. In order to investigate the copper distribution and the distribution of other heavy metals, as well as possible corrosion of the catalyst metals ruthenium and platinum, the catalyst layers were scraped off after the electrochemical experiments and subjected to element analysis by ICP-OES (ZCH).

The element analysis indicated an average ruthenium loss in the anode of 15 % or 0.13 mg/cm² of the original concentration. 90 % (0.12 mg/cm²) of this quantity of ruthenium was recovered in the cathode, which consisted of a pure platinum catalyst before operation. During operation, there was therefore significant ruthenium corrosion in the anodes and a migration of the ruthenium through the membrane to the cathode. The changes measured in the catalyst composition hold for the whole mass of the catalyst. Since ruthenium corrosion and deposition also occur on the surface of the catalyst particles, the effect is considerably greater and leads to high overvoltage losses at both electrodes.

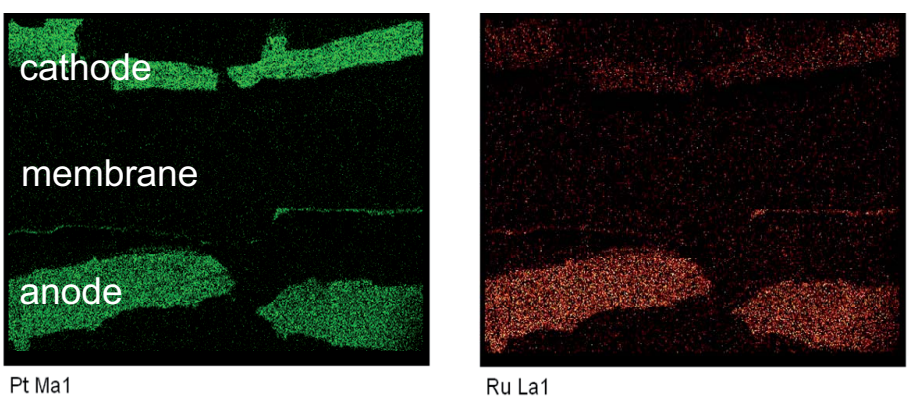
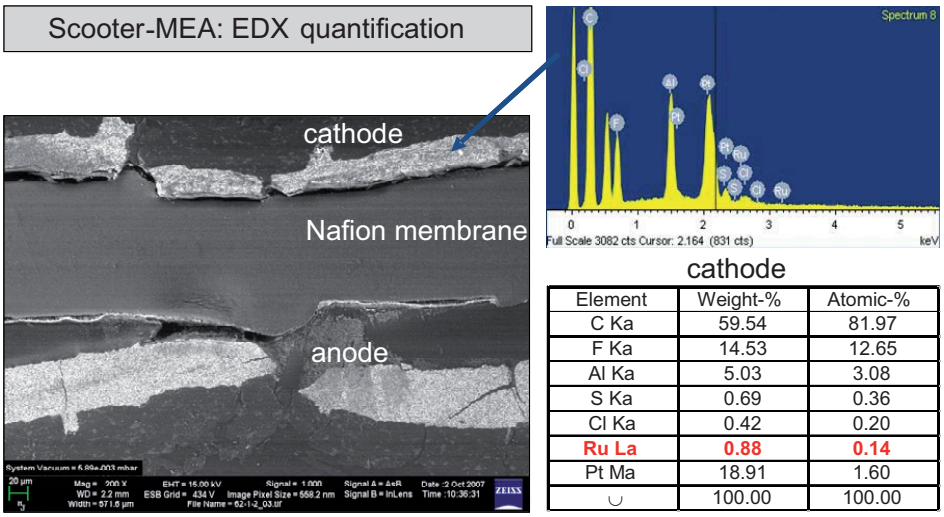


Fig. 40: Platinum and ruthenium mapping (EDX) on a cross section of an aged scooter MEA

The migration of the corroded ruthenium from the anode to the cathode was investigated by preparing cross sections of MEAs aged by operation, followed by SEM/EDX analysis. The EDX mapping in Fig. 40 qualitatively shows the presence of ruthenium in the cathode (Fig. 40, top right). Ruthenium is relatively evenly distributed in the cathode. In comparison, the membrane was found to contain no ruthenium or the levels were below the detection limit. The quantitative analysis of the EDX signals for the cathode is shown in Fig. 41. The Pt:Ru mass ratio of 21 agrees well with the range of values of 10 – 22 ascertained in the element analyses (see Fig. 40).



cathode

Element	Weight-%	Atomic-%
C Ka	59.54	81.97
F Ka	14.53	12.65
Al Ka	5.03	3.08
S Ka	0.69	0.36
Cl Ka	0.42	0.20
Ru La	**0.88**	**0.14**
Pt Ma	18.91	1.60
◡	100.00	100.00

Fig. 41: EDX quantification for the cathodes of an aged scooter MEA

In the case of the metallic contaminants, only the copper and zinc content in the electrodes increased in comparison to the unaged MEAs. For copper, there is indeed a correlation between metal content and MEA performance. The performance decreases with increasing copper content in the specimen and the copper concentration is consequently lower in the more powerful right-hand MEA region (see above).

Electrochemical degradation experiments on single cells: In different stacks, significant degradation was also determined in the past when they were turned off. This is the reason why shutdown experiments were conducted on single cells for different critical operating conditions. Two critical operating conditions, namely the addition of chloride and parasitic currents, were combined with each other. Chloride is found in the anode effluent and in the stack materials themselves (see above). It facilitates the corrosion of the noble metal catalyst by complexation.

The shutdown behavior of a stack indicates that parasitic currents are present in the stack. Once it has been shut down, the cell voltage initially increases and subsequently decreases to almost 0 V (Fig. 42). This can be explained as follows. The consumption of residual methanol in the anode causes the methanol permeation to decrease and the potential in the cathode to increase (Fig. 42: increase in cell voltage between 5 and 16 h). Charge equalization occurs as a result of parasitic currents (see below) between the cathode of a stack MEA and the anode of a neighboring stack MEA. This equalization leads to the anode taking up the cathode potential, which therefore causes the anode potential to increase (drop in cell voltage between 20 and 35 h Fig. 42). At the same time, this means a high overvoltage at the anode, which could lead to catalyst corrosion, particularly ruthenium corrosion. This agrees with the findings of strong degradation, even when turned off, and the ruthenium corrosion established by the element analyses.

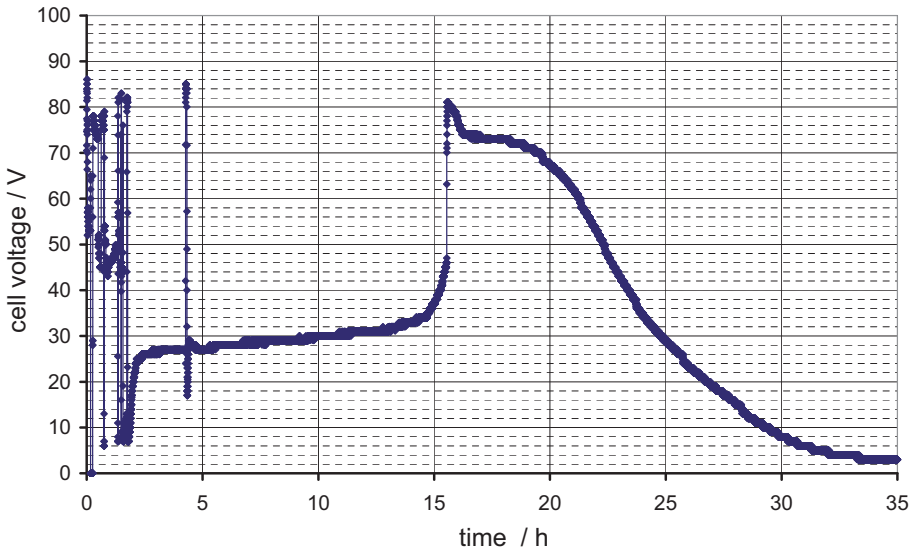


Fig. 42: Stack voltage during a shutdown measurement, 100-cell stack

A parasitic current in a stack is an inadvertent, proton-conducting connection between the anodes and cathodes of neighboring MEAs, which are electrically connected by the bipolar plates. As the bipolar plate functions as the electron-conducting connection between these electrodes, the parasitic proton-conducting connection therefore closes the electric circuit between these electrodes, and an (undesired) charge transfer occurs, which can lead to an increase in anode overpotential as described above. In terms of different parasitic sources, leaks in the bipolar Sigraflex plate can be particularly problematic. The large surface and low density means that even a small number pores could cause a parasitic current when the pores are filled with weakly acidic proton-conducting methanol solution (Fig. 43).

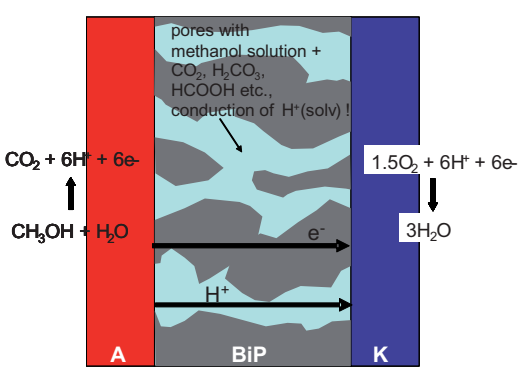


Fig. 43: Sigraflex bipolar plates as a source of parasitic current

In single-cell experiments, a parasitic current can be simulated by connecting a resistance, in other words a load, between anode and cathode. Current flows between the electrodes until

the educts (methanol, oxygen) have been consumed. Should increased anode overvoltages occur during these experiments, this effect would have to be enhanced by adding chloride.

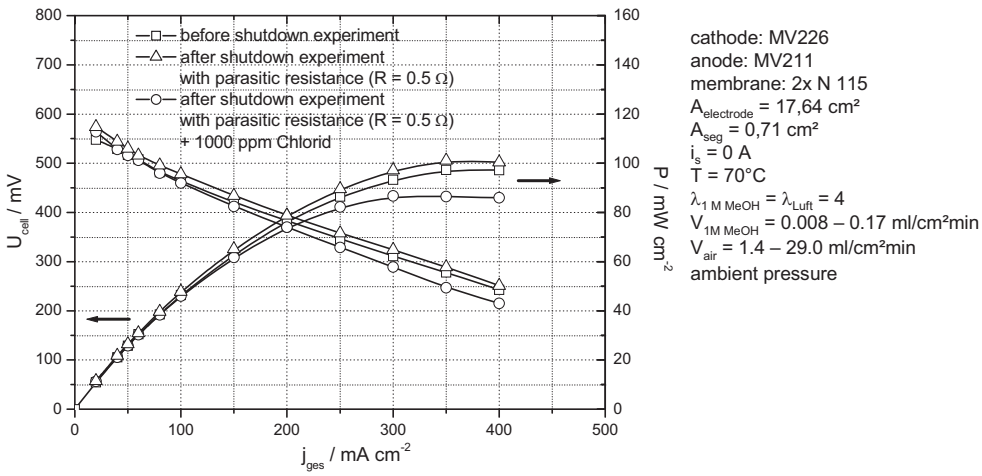


Fig. 44: Cell voltage and electrical power versus total current before and after shutdown experiments with parasitic resistance and the addition of chloride

The experiments were each conducted for a period of 24 h at 70 °C and the cathode was flushed with air. Before each experiment, the anode was rinsed with either pure or chloride-containing methanol solution and the flow of methanol was stopped during the shutdown experiment. The performance characteristics of the MEA before and after the shutdown experiments in Fig. 44 show that the parasitic currents only lead to significant performance loss when combined with the addition of chloride.

3.1.2.2 MEA fabrication

At the moment in IEF-3, MEAs are fabricated mechanically by pressing two GDEs with a membrane. The fabrication of CCMs has been established on a laboratory scale and the first tests on fabricating CCMs using machines were successful. By pressing these CCMs with gas diffusion media, MEAs can also be fabricated. As both methods of fabrication each have specific advantages depending on the materials to be processed and the effects to be examines, it makes sense to develop both methods in parallel. When fabricating MEAs using GDEs, the GDE can be modified by rolling before pressing with the membrane. For cathodes fabricated on tissue, the voltage can thus be increased by 10 mV for the full current-voltage characteristics (Fig. 45).

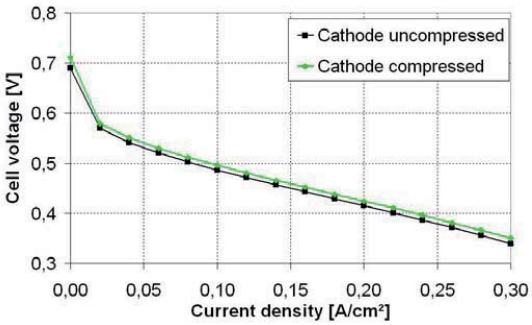


Fig. 45: Voltage increase after rolling the cathode (70 °C, anode: 1 M MeOH 0.21 ml/cm²/min, cathode: air 37 ml/(cm²min))

3.1.2.3 Stack development

Practical work on stack development can be broken down into the following fields: layout, design, fabrication, assembly and testing with the aim of developing high-performance DMFC stacks with long-term stability, which can be operated with low excess air. Fig. 46 provides an overview of the topics involved. The individual fields of work are divided into their respective subfields.

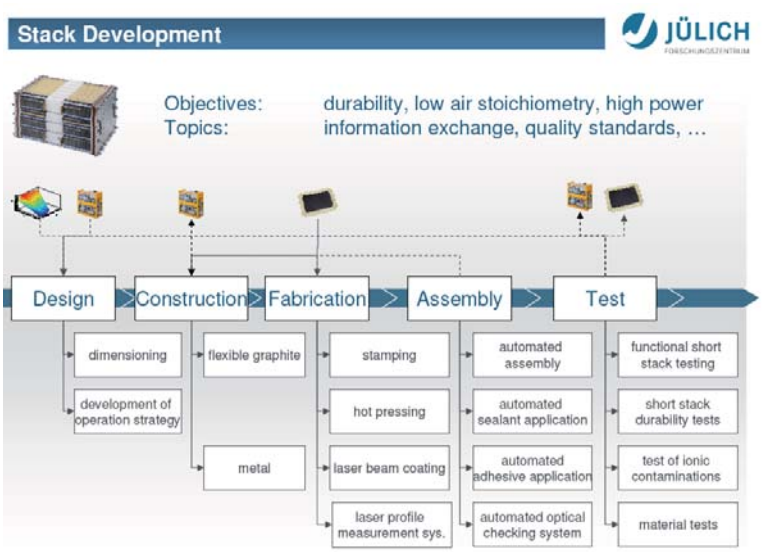


Fig. 46: Objectives and topics of the DMFC stack development group

With regard to the further development of DMFC stacks, the stack design was tailored to the specific conditions in the battery tray of a forklift truck (Fig. 47). The adjustment involved enlarging the channel cross section on the cathode side in order to reduce pressure losses in the through-flow and elevating the connectors in order to improve the mechanical stability.

The cross section of the supply channels on the anode side was also enlarged, which led to a more even distribution of media across the single cells. This alteration makes it possible to attach the embedded system in the middle of the stack to an end plate, which is advantageous in terms of the ordering of the peripheral components. The reduced number of tie rods allows the cathode exhaust to be altered to meet the requirements of multiphase material transport.

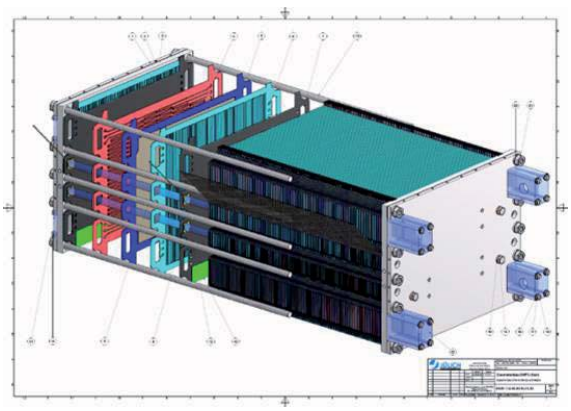


Fig. 47: Graphitic DMFC stack design 2008

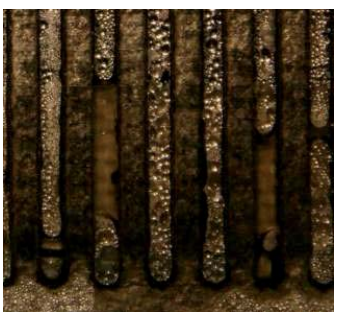


Fig. 48: Water drops in the cathode exhaust

In order to successfully implement the stack as a system, particular attention must be paid to stable operation for low excess air and low pressure losses in the range of a few millibars (< 2 mbar). This necessitates an in-depth investigation of multiphase flow at the cathode and an understanding of the transport mechanisms, particularly those in the exhaust area. Studies on transparent cells made it possible to optimize this area to such an extent that the outflow was not blocked by water in the liquid phase (as shown in Fig. 48).

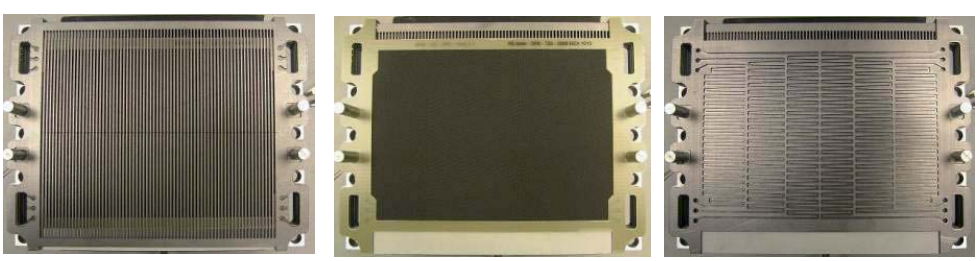


Fig. 49: Assembling a short stack with a new cell design

The new cell design was tested within the framework of trials on short stacks. The use of novel assembly aids further improved the dimensional compliance of the short stack. This is vital for the homogeneous distribution of the fuel. Fig. 49 shows photos of stack assembly in the new cell design. Beginning with the flow distributor on the cathode side on the left, the MEA is shown in the middle, followed by the flow distributor on the anode side on the right.

Improved dimensional compliance during assembly, modifications in the cathode exhaust, and the further development of the MEA made it possible to reduce excess air on the cathode to values corresponding to a stoichiometric factor of approx. three (in relation to the fuel). Fig. 50 shows the voltage characteristics of single cells in a short stack under these operating conditions. Cyclical intervention in terms of supply allows the stack to be operated at a higher mean voltage level. Differences in cell voltage when power is supplied through the cathode are 10 ml/(cm² min) at approx. 30 mV.

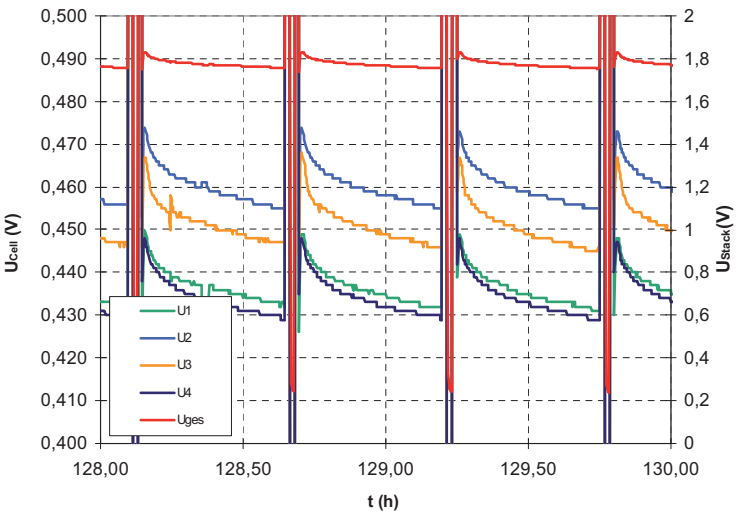


Fig. 50: Cell voltages in the short stack at V_K = 10 ml/(cm² min) @ 0.15 A/cm²

Within the framework of studies on alternative stack designs, a bipolar metallic design was improved in cooperation with industrial partners. It involves a design that enables a very space-saving setup with moderate pressure loss on the cathode side. Activities were pursued in cooperation with the Fraunhofer Institute for Laser Technology in Aachen and the GRAEBENER GROUP in Netphen-Werthenbach as part of a BMBF-funded project (reference no.: 01RI05084).

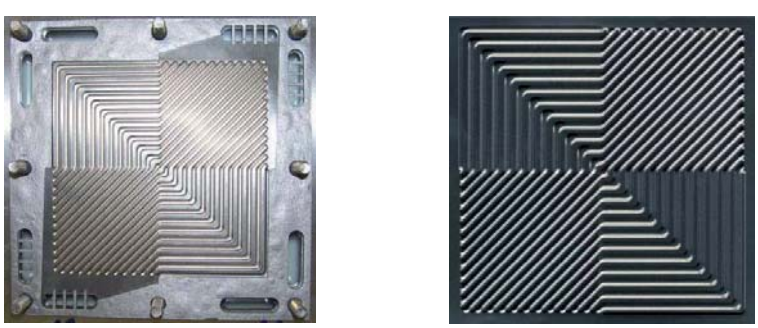


Fig. 51: Metallic stack design: bipolar plate with sealing element (left), flow distribution structure (right)

Fig. 51 is a picture of the stack design developed within the framework of the project. The flow distributor is pictured on the left in combination with a graphitic sealing element, while a detailed image of the bipolar plate with a flow distribution structure shaped by means of hydroforming is shown on the right. The flow distribution structure chosen is suitable for use both on the anode as well as on the cathode.

In addition to the use of metallic material, a new laser coating technique was developed for bipolar plates. When a corrosion-resistant base material is used, the SLM technique (selective laser melting) can be applied to coat electric functional surfaces with gold or other metals in a very economic manner.

Impact of contaminants

As part of a PhD thesis, a method was developed to systematically and thoroughly test for ionic contaminants in the anode circuit and to investigate the impact they have on the performance of fuel cells. With the aid of the results obtained, an optimized test rig was constructed to investigate contaminants. The rig can be assembled quickly and therefore allows a higher throughput. This test device can now be used to determine admissible limits for the DMFC in terms of operation with no appreciable degradation.

3.1.2.4 System development and verification

DMFC systems technology focuses on the development of concepts, the layout, design, construction and testing of fuel cell systems in relation to the respective application. Another priority is the analysis of different hybridization concepts. Above all, this comprises investigating how the DMFC stack and the energy storage unit should be connected to each other, and what type of energy storage unit (battery and/or supercap) is most suitable for each application.

Hybridization and system design

During the course of the project “Development of economic DMFC energy systems of the kW class with long-term stability for forklift trucks”, long-term measurements were taken of a representative user of forklift trucks in order to generate data on realistic driving cycles (cf. Fig. 52). Driving cycles determined in this manner can be used as input for design calculations with the aid of simulations for the DMFC stack and the battery on the one hand, and as input for measurements on a hybridization test rig on the other.

The average power, which depends on the driving cycle, is important when it comes to designing fuel cell stacks. In order to keep the energy storage unit at a predefined state of charge, the fuel cell stack must at least provide the average power as utilizable power. For a selected hybridization (stack, DC/DC converter and energy storage unit connected in parallel), the actual stack performance taking account of peripheral consumption, losses in the DC/DC converter and losses in the energy storage unit can be calculated as:

$$P_{stack} = P_{average} + P_{losses,battery} + P_{periphery} + P_{losses,DC/DC\ converter}$$

Characteristics of the driving cycle, such as shutdown and driving times, are also taken into account.

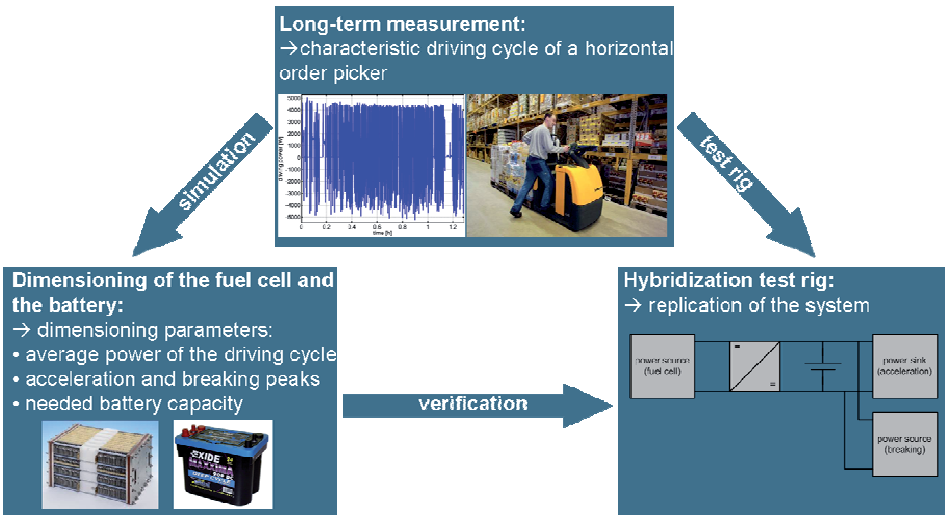


Fig. 52: Long-term measurements as input for design calculations and test rig measurements

The battery design depends on the one hand on the maximum current load, which is determined by the driving cycle, and on the other, on the required battery capacity. The required battery capacity is determined from the power of the stack and other system-related conditions, such as the warm-up phase for the DMFC stack.

In the hybridization test rig (cf. Fig. 53), which allows the planned hybrid system to be reproduced, the determined driving cycles were used to test different hybridization concepts. These measurements were then used to verify the results of the design calculations described earlier.

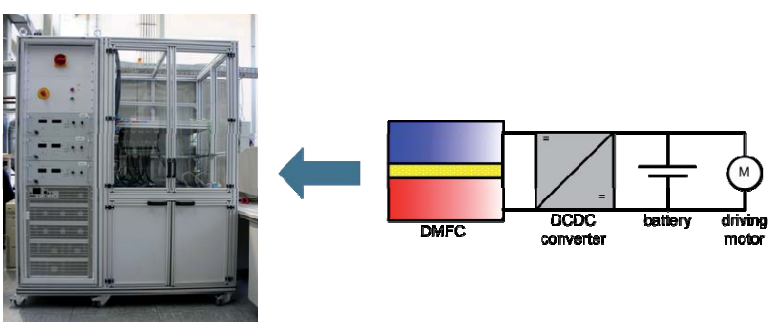


Fig. 53: Hybridization test rig

The next step involves selecting a battery that is suitable for storing energy. The lead-acid battery used in the first DMFC V3.1 prototypes was subjected to degradation tests at the Institute for Power Electronics and Electrical Drives (ISEA) at RWTH Aachen University (cf. Fig. 54). Under the same operating conditions that exist in the planned application, these tests revealed that increased degradation occurs in the form of a loss of capacity.

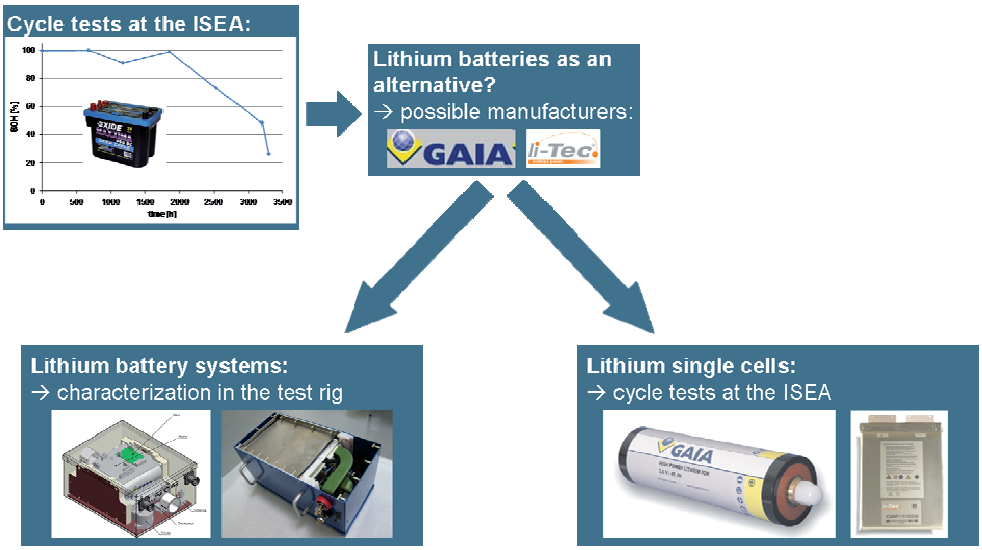


Fig. 54: Selection of suitable batteries for use as energy storage units

The project will go on to investigate whether lithium technology represents a suitable alternative. Systems and single cells from two manufacturers were acquired for this purpose. They were chosen on the basis of the battery specifications from the design calculations. The systems will then be tested in the hybridization test rig as described above. The single cells will also be subjected to degradation tests at ISEA analogous to the lead-acid batteries.

System packaging

The aim is to accommodate the complete energy system for the forklift truck in the battery tray. Fig. 55 shows the preliminary CAD sketch and the subsequent implementation of the first DMFC V3.1 system. In addition to the main components of a DMFC stack (maximum power: approx. 1.5 kW), the methanol tank (volume: 12 l, range: approx. 12 h), the condenser (water self-sufficiency up to an external temperature of 35 °C) and the hybrid battery (capacity: approx. 1 kWh), a large amount of space was required for the electrical control system and data logging.

The successor system DMFC V3.3 (due to be completed in 2009), which represents the further development of DMFC V3.1 in cooperation with an industrial consortium, comprises the following major changes:

- Increase in tank volume to 20 l. This brings us closer to achieving the goal of being able to operate a forklift truck for three full shifts in a warehouse on one full tank. This represents a significant advantage in comparison to conventional battery systems.
- Improvement in the temperature distribution in the battery tray. By means of a suitable air circulation system, the process heat created in the tray is directed outside.

– “Tailor-made” electronic components (control system with integrated data logging, DC/DC converter, cell voltage monitoring unit) developed at Jülich for a compact setup.
– Concepts for reducing degradation in the stack when it is shut down (system for shutting off the cathode, cyclical back-feeding of methanol).
– Improved control system and monitoring unit. The use of additional sensors for air mass flow, methanol concentration and temperatures should allow more robust and reliable system operation.

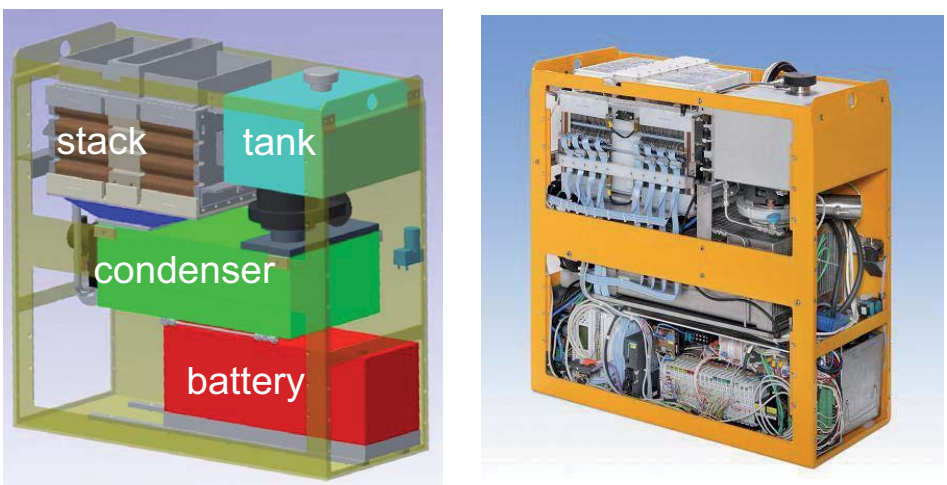


Fig. 55: Planning and constructing the system configuration for DMFC V3.1

Emissions and emission reduction

The use of methanol (in addition to the formation of CO_2) leads to emissions of methanol and degradation products from methanol oxidation in the exhaust gas of the DMFC (anode and cathode exhaust gas). This can be a critical factor, especially when a number of forklift trucks are in operation simultaneously in warehouses and the specified limits (e.g. MAC values) are exceeded.

IEF-3 began the first continuous emission measurements of DMFC exhaust gases in 2008. Fourier transform infrared spectroscopy (FTIR) is used for this purpose. The main objective of these studies is to determine the major exhaust gas components and the concentrations as a function of system operating parameters and the age of the stack.

Fig. 56 shows measuring technology from the Gasmet company. Beside the FTIR (yellow device), the unit for preparing the gas can be seen at the top of the photo (filter, heating unit (180 °C) and sample gas pump). The diagram on the right-hand side shows the first measurements of samples taken from the cathode exhaust gas, as well as from the combined cathode and anode exhaust gas, in a twenty-cell stack. The stack current density was varied here. It can be seen that in addition to methanol, methyl formate was the only

other substance that appeared to play a role in hydrocarbon emissions. Furthermore, we found clear evidence that methanol emissions came mainly from the (much smaller) anode exhaust gas. From this, we can deduce that measures for emission reduction should initially involve conditioning the anode exhaust gas. There are a number of approaches that can be used for this:

- condensation of the anode exhaust gas in a small condenser
- feeding the anode exhaust gas into the incoming air in the stack and oxidizing the methanol at the cathode catalyst
- directing the anode exhaust gas into the condenser of the cathode path

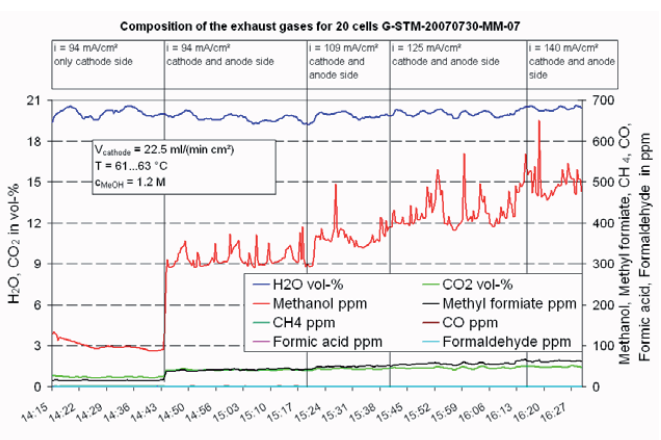


Fig. 56: Measurement setup for FTIR analysis with sample gas conditioning, first sample emission measurements in DMFC exhaust gases

The next step involves determining the emissions of the DMFC V3.3 system under realistic forklift operating conditions. Following this, a decision should be made as to whether further measures for emission reduction (e.g. catalytic post-combustion) are necessary.

3.1.2.5 Modeling

Analytical modeling is an essential tool for linking data from experiments with data from simulations. Using “simple” models that function with a few parameters, the basic behavior of fuel cells and stacks can be described. The following shows how physical considerations can be used to find out whether there is an optimal operating temperature for DMFC stacks.

The starting point for these considerations is a small volume slice of the anode channel from the middle of a DMFC stack (Fig. 57). As the surroundings of this volume element have a very similar temperature, the heat balance can be set without having to account for lateral losses (in y and z directions). The model is based on the following assumptions:

- Heat exchange with the liquid phase dominates.
- The heat generated by proton transport is very small.
- Excess methanol and oxygen is always present.

- The current density distribution is uniform along the channel.
- Evaporation occurs mainly in the MEA as its porous structure means that the active surface is very large compared to the channel.

These assumptions give rise to the following equation for the temperature of the bipolar plates.

$$-\lambda_p \frac{\partial^2 T}{\partial x^2} = \left(\frac{T\Delta S}{GF} + \eta^a + \eta^c \right) \frac{j}{h_p} + \left(\frac{T\Delta S_{cross}}{GF} \right) \frac{j_{cross}}{h_p} - \Delta H_{evap} K_{evap} \left(\frac{\varepsilon_{BL} S p_S^O}{M_w} \right) \left(p_w^{sat} - p_w \right) - H_s \frac{T - T_s}{h_c}$$

The symbols stand for the following: λ_P thermal conductivity, h_P thickness of the bipolar plates, η^a and η^c half-cell overvoltage, and the indices $_{cross}$ and $_{evap}$ stand for the methanol crossover and water evaporation.

On the basis of this equation, it can be shown that there are two main independent contributions to heat flow: heat transfer in the anode liquid, on the one hand, and the cooling effect as a result of water evaporation, on the other. Only the evaporation can completely compensate the heat generated by the electrochemical process.

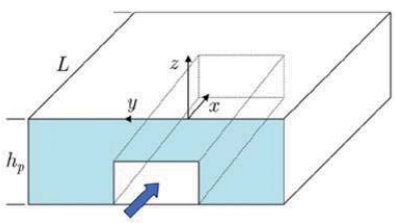


Fig. 57: Volume section from a DMFC stack with anode channel (blue arrow = flow of the H_2O/MeOH mixture)

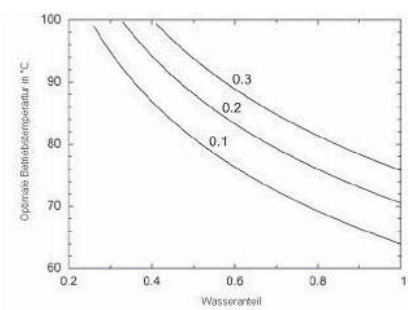


Fig. 58: Optimal operating temperature for current densities 0.1 A/cm², 0.2 A/cm² and 0.3 A/cm²

It therefore follows: the higher the current density, the higher the optimal operating temperature, as heating caused by electrochemical reactions is compensated by evaporation. Evaporation naturally depends on the water content in the stack. As the water content increases, the optimal operating temperature decreases, since a larger amount of water is thus available for cooling. This relationship is shown for three different current densities in Fig. 58.

3.1.3 Staff members and fields of activity

Name	Tel. (+49 2461-61-) E-mail address	Field of activity
Prof. L. Blum	6709 l.blum@fz-juelich.de	Head of Fuel Cells Process Engineering
J. Mergel	5996 j.mergel@fz-juelich.de	Head of Direct Methanol Fuel Cells
R. Elze	1902 r.elze@fz-juelich.de	Development of membrane electrode assemblies for DMFCs with high fuel utilization levels
Dr. A. Glüsen	5171 a.gluesen@fz-juelich.de	Performance optimization of DMFC MEAs and development of their mechanized fabrication
M. Hehemann	5431 m.hehemann@fz-juelich.de	Emission measurements on DMFC systems. Component development, setting up and operating test rigs
Dr. H. Janßen	5082 h.janssen@fz-juelich.de	Head of the DMFC System Development Group, development of components, system design, construction and testing of DMFC systems
D. Kalkreuth	2378 d.kalkreuth@fz-juelich.de	General quality management, quality assurance in the area of standardized electrochemical testing procedures
N. Kimiaie	6484 n.kimiaie@fz-juelich.de	Technical and organizational project coordination for DMFC system development, development of automated production and assembly techniques for fuel cell components and stacks
I. Konradi	4832 i.konradi@fz-juelich.de	Development of continuous mechanized processes for fabricating MEA components
Prof. A. A. Kulikovsky	5396 a.kulikovsky@fz-juelich.de	Development of analytical and numerical models of PEFCs and DMFCs, interpretation of experimental data, designing new cell and stack setups
Dr. M. Müller	1859 mar.mueller@fz-juelich.de	Head of the DMFC Stack Development Group, technical and economic optimization of DMFC stacks, selection and testing of materials for stack parts
H. Schmitz	4113 hei.schmitz@fz-juelich.de	Performance optimization of diffusion layers and catalyst layers for the DMFC

Dr. M. Stähler	2775 m.staehler@fz-juelich.de	Head of the MEA Characterization Group, standardized characterization of DMFC membrane electrode assemblies and development of new characterization procedures
C. Trappmann	5590 c.trappmann@fz-juelich.de	Development of metallic stack concepts for DMFC. Evaluation of metallic materials, investigation of degradation mechanisms
Dr. Chr. Wannek	4013 c.wannek@fz-juelich.de	Head of the MEA Development Group, development of membrane electrode assemblies for DMFC and HT-PEFC
M. Wannert	5590 m.wannert@fz-juelich.de	Development of mathematical procedures for magnetotomography, reconstruction of current density distributions using 2D and 3D models and single cells
J. Wilhelm	1573 j.wilhelm@fz-juelich.de	Systems technology development and characterization of a mobile direct methanol fuel cell unit
Dr. K. Wippermann	2572 k.wippermann@fz-juelich.de	Clarification of physical/chemical degradation mechanisms in direct methanol fuel cells
W. Zwaygardt	2109 w.zwaygardt@fz-juelich.de	Design and construction of DMFC components, setting up and operating test rigs

3.1.4 Important publications and patents

Important publications

Mergel, J.; Müller, M.; Janßen, H.; Stolten, D.

Direktmethanol-Brennstoffzellensysteme – eine Option für Flurförderfahrzeuge (Direct Methanol Fuel Cell Systems – An Option for Forklifts)

Der 4. Deutsche Wasserstoff Congress 2008 - Tagungsband, Schriften des Forschungszentrums Jülich, Reihe Energie & Umwelt Band 12, ISBN 978-3-89336-533-3, (2008) 81 - 93

This paper provides an overview of the state of the art of DMFC systems for material handling applications in Forschungszentrum Jülich and presents the results of a marketability study, which shows that the kW-class DMFC system has the best potential for commercialization in a forklift truck. The prerequisites for launching such systems on the market not only include a high power density and long-term stability, but also a competitive price level compared to existing technologies. Economic application still necessitates R&D, particularly with regard to the service life of a stack as well as control strategies and the hybridization of the DMFC energy system. The biggest challenges in developing prototypes are long-term stability, water self-sufficiency, and hybridization.

Steinberger-Wilckens, R.; Mergel, J.; Glüsen, A.; Wippermann, K.; Vinke, I.; Batfalsky, P.; Smith, M.J.

Performance degradation and failure mechanisms of fuel cell materials

Chapter 11 in: Materials for fuel cells, Edited by M. Gasik, Helsinki University of Technology, Finland, ISBN 1 84569 330 2, ISBN-13: 978 1 84569 330 5, October 2008

> 'Materials for fuel cells' is a review of developments in the area of materials for fuel cells as a major power source. After introductory chapters on the key issues in fuel cell materials research, the book reviews the major types of fuel cell. These include alkaline fuel cells, polymer electrolyte fuel cells, direct methanol fuel cells, phosphoric acid fuel cells, molten carbonate fuel cells, solid oxide fuel cells and regenerative fuel cells. The book concludes with reviews of novel fuel cell materials, ways of analyzing performance, and issues affecting recyclability and life cycle assessment.
> Fuel cells, like any other electrochemical devices, experience a loss of performance during their operational life. This is termed 'degradation' and most commonly described as a loss of cell voltage at a given operational point, which immediately translates to a loss in electrical power supplied. Fuel cell degradation can be caused by a number of factors, and it depends on the type of fuel cell in question and the materials incorporated in it. The most prominent factors influencing degradation in steady-state operation are the current and operational temperature. A second important set of causes for degradation, with often immediate and dramatic impact, are transient operation (load and thermal cycling) and operation outside the regular window of parameters (for instance redox cycling in SOFC). Finally, fuel impurities also influence the long-term performance.
> This chapter gives a brief overview of degradation mechanisms in fuel cells, concentrating on PEFC, DMFC and SOFC technology.

Wilhelm, J.; Janßen, H.; Mergel, J.; Stolten, D.

Horizontal Order Picker Driven by a Direct Methanol Fuel Cell

Symposium on Power Electronics, Electrical Drives, Automation and Motion 2008 (SPEEDAM 2008), Ischia (Italien), 11. – 13. Juni 2008, ISBN 978-1-4244-1663-9, S. 832 – 836, http://dx.doi.org/10.1109/SPEEDHAM.2008.4581324

> Direct methanol fuel cells (DMFCs) directly convert liquid methanol into electric energy. In addition to the very high energy density of methanol, the DMFC is characterized by easy handling and unproblematic refueling. Direct methanol fuel cells are attractive for various applications, for example as replacements for batteries or accumulators, since DMFC systems permit longer operating times due to the high energy density of methanol. A market analysis was done to find the best application for a later commercial realization. The result of this market analysis shows the best potential for systems in the material handling sector. Therefore a DMFC system was designed for a horizontal order picker. In this paper, the system will be described in the field of process engineering and hybridization. With regard to hybridization, the used energy storage will be a main focus. The control strategy of the DMFC system is also described.

Kulikovsky, A.A.

Efficient parallel algorithm for fuel cell stack simulation

SIAM J. Appl. Math. (2008, in press)

A planar fuel cell stack is a layered structure consisting of repeated modules: membrane-electrode assemblies (MEAs) separated by bipolar plates (BiPs). The distributions of voltage and temperature over the BiP volume can generally be described by 3D Laplace equations. However, the thickness of BiPs is much smaller than the in-plane size. This makes it possible to reduce the 3D Laplace equation to a 2D Poisson equation and to develop an efficient parallel algorithm for stack simulation. In the simplest variant, each individual module “MEA + BiP” is solved on a separate processor. Typically, the number of cells in a stack varies between 10 and 100. This algorithm is thus most suitable for small-scale and medium-scale parallel machines. A much faster method is to cut each module into a number of stripes and to solve each stripe on a separate processor. Numerical tests have shown that even with 8 stripes per module, this method solves electric problems roughly ten times faster than expected. Evidently, the striping algorithm provides much faster convergence of the iterative Poisson solver. This can be explained by fast damping of high-frequency modes of potential in the iteration process. This algorithm may open up possibilities for the fast simulation of real 100-cell stacks using massively parallel machines.

Important patents

Patent applications:

Principal inventor	PT	Description
Dr. M. Müller	1.2262 PCT	Fuel cell system and process for operating the same
M. Schonert	1.2291 EP	Structured electrodes for use in a fuel cell
Dr. C. Schlumbohm	1.2295 EP	Direct alcohol fuel cell stack with a carbon dioxide separator
Prof. Dr. D.U. Sauer	1.2318 PCT/EP	Method for electrochemical activation of fuel cells
Dr. M. Müller	1.2326	Exhaust gas purification system for a fuel cell or a fuel cell stack
Dr. M. Müller	1.2330	Fuel cell system and method for regulating a fuel cell system
Dr. M. Müller	1.2331	Fuel cell system and method for regulating a fuel cell system
Dr. M. Stähler	1.2342	Device and method for calibrating a carbon dioxide sensor
Dr. H. Janßen	1.2398	Heat exchanger

Patents granted

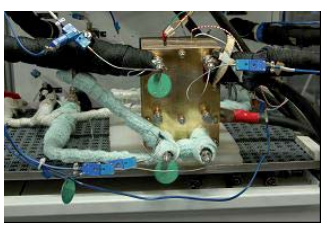
Principal inventor	PT	Description
Dr. J. Divisek	1.1462	Production of gas diffusion electrodes by electrolytic deposition of a catalyst
Th. Bewer	1.1818 EP	Fuel cell stack
Prof. H. Baltruschat	1.1854	Fuel cell stack with circuit
H. Schmitz	1.1982	Layered structure for a gas diffusion electrode, methods producing and applying this layered structure
Th. Bewer	1.2001	Bipolar plate for a fuel cell and fuel cell stack
Dr. J. Bringmann	1.2067 EP	Cathode for a direct methanol fuel cell and operation procedure for the same
Dr. C. Schlumbohm	1.2072	Catalyst layer, suitable catalyst ink, and fabrication technique for the same

3.2 Key topic: high-temperature polymer electrolyte fuel cells

3.2.1 Objectives and fields of activity

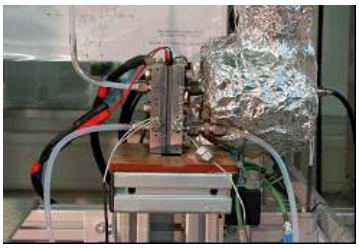
Commercial vehicles, construction machines, ships and aircraft will continue to be run on diesel and kerosene in the long term. Substantial energy savings can be made by increasing electrification as this results in a more efficient on-board generation of power. From a practical point of view and in the interests of the end user, these auxiliary power units (APUs) must be run on the fuel that is already available on board. This means that these “middle distillates” must be reformed. If the high-temperature polymer electrolyte fuel cell (HT-PEFC) is combined with an appropriate reforming technology on board, it becomes possible to efficiently generate electricity, even when the engine is not running.

The HT-PEFC, based on polybenzimidazole membranes doped with phosphoric acid, has a typical operating temperature of 160 °C. As a result of the high temperature level, it has a high CO tolerance, which means that it is particularly suitable for operation in combination with reformers. Compared to Nafion-based polymer electrolyte membrane fuel cells, water is not required for the ionic conductivity of the membrane; therefore the gases do not need to be humidified. Another advantage of HT-PEFC technology is that due to the high temperature difference between the stack and the ambient temperatures, cooling can be designed in a much more compact manner than is necessary in classical PEMFC systems.



However, for all these advantages, prevention measures must be in place to ensure that the acid is not discharged from the membrane. Operating conditions that could create liquid water in the cells should be avoided. Furthermore, it was shown that the membrane resistance increases significantly at a temperature below 60 °C. Operation in low temperature ranges should therefore be avoided. This has been taken into account by operating strategies and the specific areas of application.

Since 2005, research projects have been pursued at IEF-3 in the field of the HT-PEFC. These include activities in the field of electrode development, on the one hand, and activities related to stack development, on the other. Due to positive experience with this technology and the appraisal of possible application potential, it was decided to establish this area as a new key topic within fuel cell research. Following this decision, the new High-Temperature Polymer Electrolyte Fuel Cells Group was set up in 2008. Currently, the group focuses on three topics. These are electrode development, stack development in the 5-kW power range, and modeling and simulation.



Due to the institute's many years of experience in SOFC and DMFC research and development, synergy effects exist which will accelerate HT-PEFC development. Fundamental methods in electrode, cell and stack technology, which have already been established in the DMFC area, were adapted. With respect to process engineering simulations of the design of cells and stacks, recourse was made to experience in the SOFC area. This allowed the new area to be effectively expanded into a new key topic over the last few years.

This process was supported by sizeable investments in the laboratory. Some of the existing test rigs were modified. Furthermore, two new test rigs specially designed for HT-PEFC technology were purchased and put into operation. These two test rigs now cover stack powers that range up to 5 kW_{el}.

3.2.2 Important results

3.2.2.1 Electrode and MEA development

Based on the results of the last few years, intensive work will continue on electrode and MEA development. The membrane material used is ABPBI (poly(2,5-benzimidazole), which is supplied by a company (FuMA-Tech GmbH).

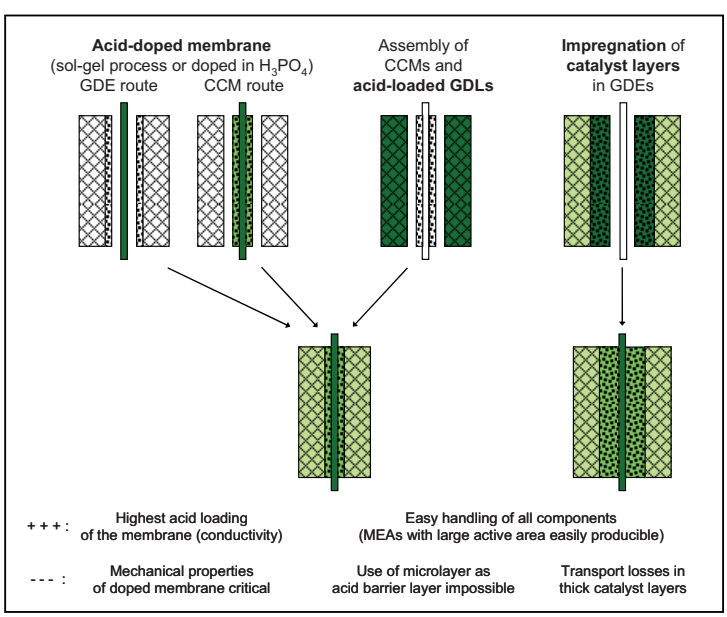


Fig. 59: Concepts for introducing phosphoric acid into HT-PEFC MEAs

ABPBI, similar to PBI (poly(2,2′-(m-phenylene)-5,5′-bibenzimidazol), which is used in commercial MEAs, is characterized by a high absorption capacity for phosphoric acid and

thus has the potential for high proton conductivity. In the non-cross-linked state, however, ABPBI is soluble in phosphoric acid. This therefore excludes a sol-gel process for the direct fabrication of membranes doped with phosphoric acid.

The strong swelling of the membrane when it absorbs acid (strong anisotropic volume change: thickness increases by a factor of three while area increases by only 4 %) makes the doped membrane difficult to work with (for a coating with catalyst or for pressing with gas diffusion electrodes). For this reason, a process was further developed in IEF-3, which allows acid to be fed into the membrane via the electrodes and thus simplifies the fabrication of MEAs with large cell areas (Fig. 59). The advantages of the method developed in IEF-3 (Fig. 59, right) is the easy-to-realize continuous fabrication of gas diffusion electrodes (GDEs).

Impregnation with 6 mg H_3PO_4 per cm^2 of electrode area at the anode and cathode would be enough to ensure maximum conductivity of the pure membrane in case all of the acid was to pass through the catalyst layer into the membrane. However, doping with 10 mg H_3PO_4 per cm2 has shown that this is insufficient: cell tests revealed a maximum power density of 110 mW/cm^2 instead of the expected 250 mW/cm^2 (Fig. 60). Only with a high excess of phosphoric acid was the expected power density achieved; a significant proportion of phosphoric acid remained in the catalyst layer and ensured sufficient proton conductivity.

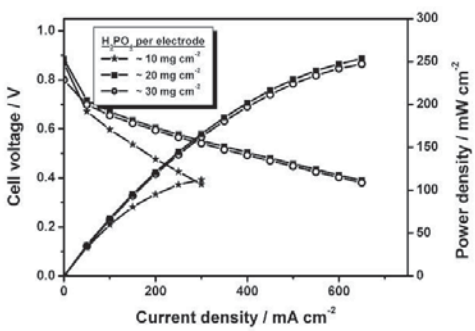


Fig. 60: U(j) curves (160 °C, H2/air) of MEAs with different PTFE contents in the catalyst layer

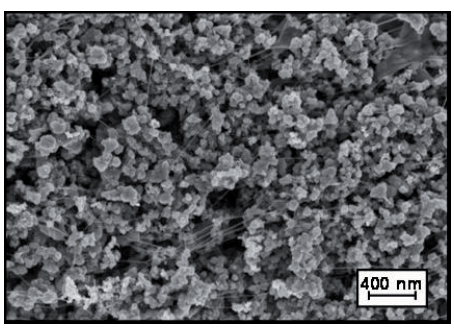


Fig. 61: SEM micrograph of an electrode with 20 % Pt/C and 40 wt% PTFE

The catalyst layer is currently applied using a blade process, whereby the optimization of the composition and fabrication of the coating dispersions and the coating technique ensure an ideal fine dispersal of catalyst and polymeric binder (PTFE) in the electrode (Fig. 61). Alternative coating techniques will be evaluated in IEF-3's new fabrication facility in the future.

Although the assembling of MEAs and the related redistribution of phosphoric acid is performed without a hot press process directly in the cell, MEAs can deliver current shortly after the first time they are heated to operating temperature. After only 12 min, for example, a current density of 200 mA/cm^2 is achieved at a cell voltage of 600 mV (Fig. 60), which finalizes the coarse dispersal of the acid. After around 70 to 100 hours, the MEA delivers maximum power. From this, we can conclude that after this time, the fine dispersal of the

acid has been completed inside the MEA. We did not detect any effect of this fast insertion procedure on lifetime.

In addition to continuously optimizing the design and fabrication of MEAs, fundamental investigations will be conducted in the future in order to describe cathode losses (which are high compared to classical PEFCs), with the aim of increasing the typical operating voltage of the HT-PEFC from the current value of 550 – 600 mV to at least 650 mV in the medium term and thus ultimately increasing the efficiency of the system.

3.2.2.2 Stack development

The objective of stack development is to design, construct and test HT-PEFC stacks with a power of 5 kW. Development focuses specifically on applications in the area of on-board power supply, as the HT-PEFC is particularly suitable for such applications when combined with a reformer. The HT-PEFC becomes even more relevant when the fuel that is already in the vehicle can be used. As both diesel and kerosene will continue to be used in the future, the stacks are designed for reformate gas typically containing 33 % hydrogen and 1 % carbon monoxide in wet reformate. Due to the operating temperature between 140 °C and 180 °C, stacks are capable of withstanding the high CO content in the reformate gas. Stacks are designed for operation at ambient pressure and, thanks to the use of the PBI membrane doped with phosphoric acid, they require no external humidification, which leads to a simplified system layout. Both in-house MEAs and MEAs from cooperation partners were incorporated into the stacks.

Within the framework of stack development, different stack designs were tested. An HT-PEFC stack of the 100-W class was developed and tested back in 2006. Based on the results achieved and the experience gained in the field of DMFC stack development, new designs were created. For the 5-kW power class, on the basis of the 100-W stack, a concept was developed whereby the electrochemically active areas were strictly separated from the oil cooling areas. The advantage of this design is that single cells can be replaced without any coolant seeping into the electrochemically active areas. Furthermore, leakages in the area where the coolant is distributed through externally located manifolds can be detected immediately by an optical inspection. The bipolar plate unit is therefore composed of three components, as can be seen in Fig. 62: two reactant bipolar plates and the separate cooling plate unit. The bipolar plates are composed of graphitic materials with milled flow fields, while the separate cooling cells are fabricated from metal. The stack has an active cell area of 320 cm^2. Around 60 cells are required when operating the stack with diesel reformate in order to achieve a power of 5 kW.

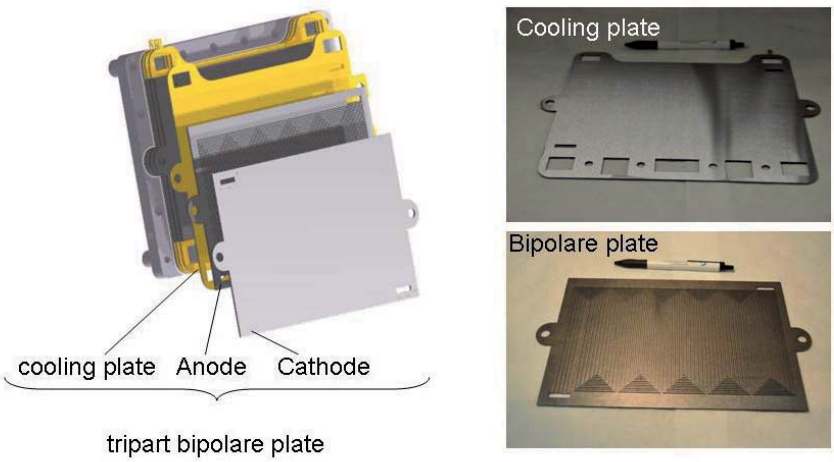


Fig. 62: Stack design with separate cooling and reaction areas

With regard to the development of another stack design based on purely graphitic materials, the primary emphasis was on a simple fabrication technique. This stack is also supplied with reformate, which is fed into the cells with an active area of 200 cm² via the manifolds, which are integrated into the bipolar plates. The cooling channels are also integrated into the bipolar plates and are located on the back side of the cathode. The bipolar plate unit composed of reactant distribution and cooling therefore consists of two parts (Fig. 63): the anodic and cathodic bipolar plates. This design allows both air and conventional thermal oil to be used as coolants. The cooling side can only be sealed at the moment using O rings made of FKM or adhesive glue. With regard to automating and simplifying fabrication, adhesive glue is preferred in the long term. As a result of its compact construction, a stack of the 5-kW class can be realized from a number of modules with around 10 cells per module. This means that if a module should fail, the stack will continue to operate with a lower power.

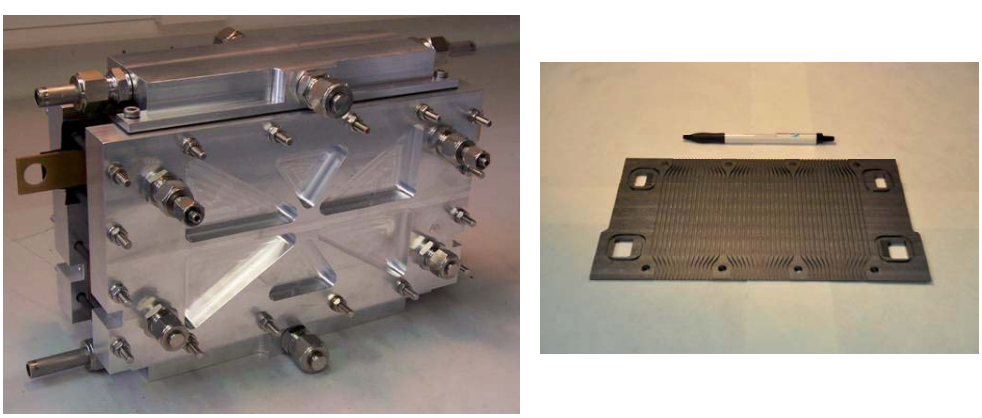


Fig. 63: HT-PEFC stack with an active area of 200 cm^2 for air and liquid cooling

3.2.2.3 Modeling and simulation

When modeling fuel cell stacks, strong nonlinear coupled process should be taken into account on different spatial and time scales. These different scales prevent the use of a single modeling approach. It therefore makes sense to choose a suitable model and simulation tool for each individual problem. On the one hand, activities focus on explaining basic physical and chemical relationships, while on the other, development work on new fuel cells and cell stacks is encouraged. In the future, intensive cooperation with the institute's new physicochemical analysis laboratory will form the basis for explaining the influence of structure on the properties and performance of fuel cell components using both mathematical and experimental methods.

The core component of every fuel cell is based on the combination of membrane electrode assembly (MEA) and gas diffusion layer (GDL). In the former, the electrochemical processes occur, which ultimately determine the mass and energy transfer in the cell. This combination of MEA and GDL is composed of a mixture of different materials, which exhibit a complex structure both on the nm scale (electrode) as well as on the µm scale (GDL). In addition to tissues, nonwoven fabric and papers are used as GDL materials in the HT-PEFC. The last two material classes, in contrast to tissues, have a more random fine structure. As expected, MEAs with different substrates behave differently. Explaining this and gaining a basic understanding of the structure and the influence of structure on the properties are the aims behind a cooperation with the Institute of Stochastics at Ulm University (BMBF, 03SF0324). The microstructure is described quantitatively using stochastic methods. Structure parameters are extracted from 3D synchrotron tomographic images and 2D SEM micrographs. These are used to build a statistically equivalent 3D layer model of a GDL by means of a Poisson line tessellation and subsequent dilatation of the lines. The results of the model are shown in Fig. 64. The white areas represent the binder, which is preferentially found between the filaments.

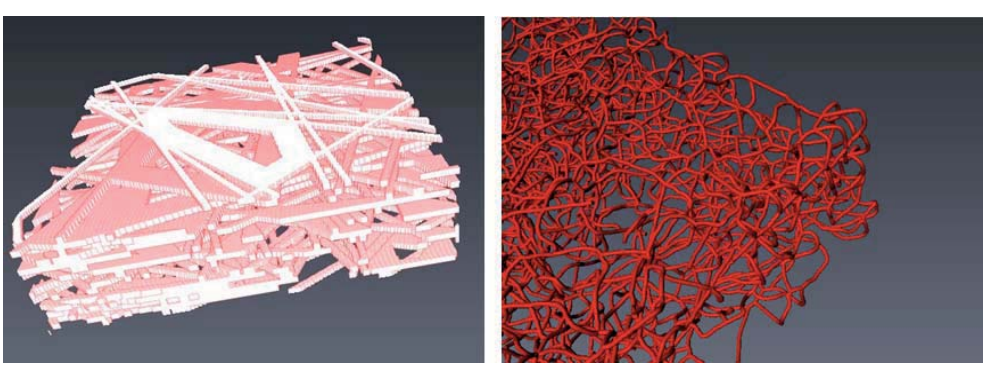


Fig. 64: Layer model (left) and graphical representation of the pore space (right)

The layer model forms the basis for calculating the structural properties, which are extremely important for mass transfer (for example, coordination numbers and tortuosity). In order to determine the characteristic structure of the pore space, the latter is derived as a graph from the model (Fig. 64), whereby the pore space is weighted for each segment of the graph. This allows the "transport capacity" of individual pore segments to be taken into account. The

tortuosity is generally described as the effective path length of the gas through the material compared to the material thickness (Fig. 65). Within the stochastic model of the fine structure, tortuosity is defined as the shortest path from one side of the GDL to the other side along the edges of the graph. In addition to the mean tortuosity, the tortuosity distribution was also determined. Instead of a single value, we thus have a distribution function, which contains information on the structure. Fig. 65 compares the tortuosity distribution, calculated using the 3D synchrotron data and the fine structure model, with different models in order to image the binder. It can be seen that the binder model has a huge influence on the tortuosity distribution, whereby the mean tortuosity in the cases illustrated is comparable.

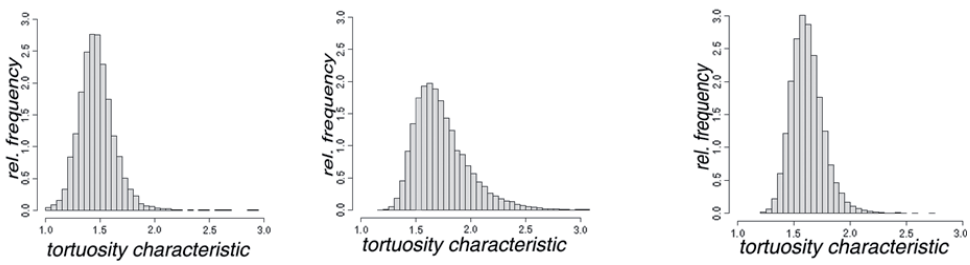


Fig. 65: Tortuosity determined using 3D data (left) from the model. Single cells completely filled with binder (middle) and cells partially filled with binder (right)

Parallel to stochastic modeling, CFD simulations (computational fluid dynamics) were performed to describe the heat and mass transfer in HT-PEFCs. CFD models are characterized by a high degree of flexibility, but their complex numerical control necessitates a huge amount of computing time. Furthermore, a large number of parameters are necessary, some of which are difficult to ascertain in experiments. CFD models, however, are an indispensible tool for the development of new cells and cell stacks. This is the reason why the development of new fuel cell models is being pursued in cooperation with the National Research Council (NRC, Canada).

In order to describe individual physical effects and their interaction with each other, analytical models are the method of choice. Using “simple” models that function with a few parameters, the behavior of fuel cells and stacks can be described. Analytical modeling is an essential tool for relating data from experiments to data from simulations. The following shows how important model parameters were derived from experimental data using an analytical model.

One of the simplest models for describing a fuel cell only has four parameters. This model is used to extract parameters from the measured current-voltage curves of an HT-PEFC. The following model assumptions were used as a basis. The oxygen reduction satisfies Tafel’s law. Transport losses in the cathodic catalyst layer are negligible. The oxygen transport in the gas diffusion layer is diffusive. The membrane is impermeable to gases. The cell is isothermal and plug flows can be assumed in the channels. Under the assumption that the losses on the anode side are negligible, after the solution of a system of conservation equations, the cell voltage can be described as follows:

$$V_{cell} = V_{oc} - b\ln\left(\frac{c_{ref}\ f_\lambda J}{c_{ox}^0 j_*}\right) + b\ln\left(1 - \frac{f_\lambda J}{j_{\lim}}\right) - R_{cell} J$$

with the symbols: Tafel slope b, exchange current density j_*, limiting current j_{lim}, function f_λ and cell resistance R_{cell}. V_{oc} is the open cell voltage; c_{ref}, c_{ox} are the reference and oxygen concentrations, respectively.

$$b = \frac{RT}{\alpha F} \quad j\lim = \frac{4FD_b c_{ox}^0}{l_b} f_\lambda = -\lambda \ln\left(1 - \frac{1}{\lambda}\right)$$

The equation for describing cell voltage consists of the four parameters b, j_*/c_{ref}, j_{lim} and R_{cell}. If the equations are written for two different stochiometries and then subtracted from each other, the result is an equation with two parameters (b, j_{lim}), which can be fitted without any problems to the difference of two measured current-voltage curves with different stochiometries.

$$V_{cell}(\lambda 1) - V_{cell}(\lambda 2) = -b \ln\left(\frac{\phi_{\lambda 1}}{\phi_{\lambda 2}}\right) + b \ln\left(\frac{j_{\lim} - \phi_{\lambda 1} J}{j_{\lim} - \phi_{\lambda 2} J}\right)$$

These parameters are used in order to determine the two remaining parameters with the original equation. In contrast to a direct numerical fitting of the four parameters, this method avoids convergence problems. The following values were determined for the parameters:

$$b : 0{,}048\ V \qquad j_{\lim} : 1{,}34\ A\ cm^{-2} \qquad j^* : \quad 1{,}5x10^{-5}\ A\ cm^{-2} \qquad R_{cell} : 0{,}26\ \Omega\ cm^2$$

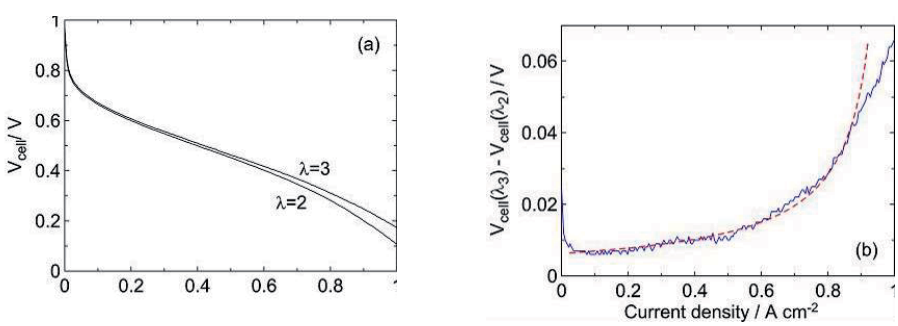


Fig. 66: (a) polarization curves determined by experiment, (b) blue line: difference of the curves from (a), red line: model

The difference between the experimental current-voltage curves and their fit is shown in Fig. 66. Fig. 67 shows the quality of the fit. The deviations at high current densities in Fig. 67 can be explained by the fact that the model assumptions are not fulfilled in this area. Based on an analytical model, reliable parameters for describing HT-PEFCs using models are thus available for the first time.

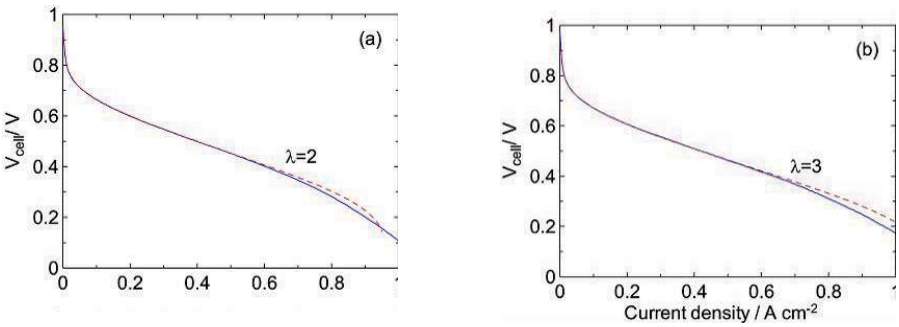


Fig. 67: **Blue lines: polarization curves determined by experiment; red lines: model for excess air of λ=2 (a) and λ=3 (b)**

3.2.3 Staff members and fields of activity

Name	Tel. (+49 2461-61-) E-mail address	Field of activity
PD Dr. W. Lehnert	3915 w.lehnert@fz-juelich.de	Head of High-Temperature Polymer Electrolyte Fuel Cells
A. Bendzulla	2177 a.bendzulla@fz-juelich.de	Development of HT-PEFC stacks, benchmarking of stack materials
D. Froning	6676 d.froning@fz-juelich.de	Modeling of fuel cells, computer science, software engineering
N. Jahani	3018 n.jahani@fz-juelich.de	Modeling and simulation of HT-PEFCs
B. Kohnen	5406 b.kohnen@fz-juelich.de	Technical support for HT-PEFC test rigs and examination of HT-PEFCs
Prof. Dr. A. Kulikovsky	5396 a.kulikovsky@fz-juelich.de	Development of analytical and numerical models of HT-PEFCs, DMFCs and SOFCs
H.-F. Oetjen	6029 h.-f.oetjen@fz-juelich.de	Development of designs for test rigs for HT-PEFCs, testing and characterization of HT-PEFCs
Dr. U. Reimer	3537 u.reimer@fz-juelich.de	Head of the HT-PEFC Modeling and Simulation Group
Dr. Chr. Wannek	4013 c.wannek@fz-juelich.de	Head of the MEA Development Group, development of membrane electrode assemblies for DMFC and HT-PEFC

3.2.4 Important publications and patents

Important publications

Wannek, C.; Kohnen, B.; Oetjen, H.-F.; Lippert, H.; Mergel, J.

Durability of ABPBI-based MEAs for High Temperature PEMFCs at Different Operating Conditions

Fuel Cells, 8 (2008) 87-95

High-temperature PEMFCs based on phosphoric-acid-doped ABPBI membranes were prepared and characterized. At 160 °C and ambient pressure, fuel cell power densities of 300 mW cm^{-2} (with hydrogen and air as reactants) and 180 mW cm^{-2} (with simulated diesel reformate/air) were achieved. The durability of these membrane electrode assemblies (MEAs) in the hydrogen/air mode of operation at different working conditions was measured electrochemically and was correlated to cell resistivity, phosphoric acid loss rate and catalyst particle size. Under stationary conditions, a voltage loss of only –25 µlV h^{-1} at a current density of 200 mA cm^{-2} was determined in a 1,000 h test. Under dynamic load changes or during start–stop cycling, the degradation rate was significantly higher. Leaching of phosphoric acid from the cell was found to be very small and was not the main reason for the performance loss. Instead, an important increase in the catalyst particle size was observed during two long-term experiments. At high gas flows of hydrogen and air, ABPBI-based MEAs can be operated at temperatures below 100 °C for several hours without a significant irreversible loss of cell performance and with only very little acid leaching.

Wannek, C.; Dohle, H.; Mergel, J.; Stolten, D.

Novel VHT-PEFC MEAs Based on ABPBI Membranes for APU Applications

ECS Trans., 12 (2008) 29-39

We report on the performance of poly(2,5-benzimidazole) (ab-PBI or ABPBI; 'AB' reflects the fact that the polybenzimidazole is formed in head-tail variety) membrane-based membrane electrode assemblies (MEA) for use as very-high-temperature PEFCs (T = 160 – 180 °C). In view of the possible future application of this special type of fuel cell – e.g. in auxiliary power units (APU) in trucks or aircraft – these MEAs were tested with a six-component gas mixture simulating the composition of a fuel gas produced by autothermal reforming of middle distillates such as diesel or kerosene after the shift reaction. The cell performances with hydrogen and synthetic reformate at different operating temperatures of the fuel cell and thus their 'CO tolerances' are presented and discussed. MEAs with an active area of 46 cm^2 were operated successfully in a prototype 10-cell stack with novel modular design.

Thiedmann, R.; Fleischer, F.; Hartnig, Ch.; Lehnert, W.; Schmidt, V.

Stochastic 3D Modeling of the GDL Structure in PEMFCs based on Thin Section Detection

J. Electrochem. Soc. ***155*** *(2008) B391-B399*

We propose a mathematical model to describe the microstructure of the gas diffusion layer (GDL) in proton exchange membrane fuel cells (PEMFCs) based on tools from stochastic geometry. The GDL is considered as a stack of thin sections. This assumption is motivated by the production process and the visual appearance of relevant microscopic images. The thin sections are modeled as planar two-dimensional (2D) random line tessellations, which are dilated with respect to three dimensions. Our 3D model for the GDL consists of several layers of these dilated line tessellations. We also describe a method to fit the proposed model to given GDL data provided by scanning electron microscopy images which can be seen as 2D projections of the 3D morphology. In connection with this, we develop an algorithm for the segmentation of such images which is necessary to obtain the required structural information from the given grayscale images.

Thiedmann, R.; Hartnig, H.; Manke, I.; Schmidt, V.; Lehnert; W.

Local Structural Characteristics of Pore Space in GDLs of PEM Fuel Cells Based on Geometric 3D Graphs

J. Electrochem. Soc. submitted

Physical properties affecting transport processes of the gas diffusion layer (GDL) in fuel cells mainly depend on the microscopic structure of its pore space. The present investigation of pore space is based on geometric 3D graphs, i.e. the complex microscopic structure of pore space is represented by a 3D graph. This representation contains essential information on the geometrical structure of the pore space, such as its connectivity. In addition, the vertices and edges of the graph are equipped with marks in order to describe the size of pores and throats at given locations. This 3D graph representation of the pore space can be used to investigate local structural characteristics of the GDL by considering local tortuosity characteristics, pore sizes, and connectivity characteristics, respectively. In particular, the notion of a local shortest path length through the pore space of the GDL is introduced, and the probability distribution of this random variable is computed. Its mean value is related to the (physical) tortuosity, which is given by the ratio of the mean effective path length through the GDL and its thickness. For a better approximation of effective path length capacity, weighted shortest paths are considered where the 'capacity marks' of the individual edges of these paths are taken into account. This comprehensive information is used to compare the microstructures of different materials with equal (mean) porosities. Since the proposed method for the construction of the 3D graph is based on 3D voxel data, it can be applied to simulated model data as well as to real (measured) 3D image data gained, for example, by means of synchrotron tomography. The stochastic 3D model for the GDL considered in the present paper is an extended version of the multi-layer model introduced in a previously published paper but includes a more flexible modeling of the binder. The dependence of the considered local characteristics of the entire GDL on the choice of the binder model is demonstrated. The presented procedure allows for a differentiation of structural properties of materials obeying the same porosity.

Kulikovsky, A.A.; Oetjen, H.-F.; Wannek, Ch.

A simple and accurate method for high-temperature PEM fuel cells characterization

J. Electrochem. Soc. submitted

A set of basic parameters for any polymer electrolyte membrane fuel cell (PEMFC) includes Tafel slope b, exchange current density j^0 of the cathode reaction, diffusion coeffcient D in the cathode gas diffusion layer and cell resistivity R_{cell}. Recent analytical models of a conventional PEMFC suggest a two-step procedure, which allows these parameters to be evaluated for high-temperature PEMFCs. The procedure requires two polarization curves measured at different oxygen (air) stoichiometries. The first step involves fitting the difference of two curves; the respective fitting equation contains b and D only. In the second step, one of the polarization curves is fitted to obtain j^0 and R_{cell} and the other curve is used to verify the results. The high quality of fitting in both steps confirms the validity and accuracy of this approach. The physical background of the method is discussed.

Important patents

Patent applications:

Principal inventor	PT	Description
Ro. Peters	1.2338	High-temperature polymer electrolyte fuel cell system and process for operating the same

Patents granted

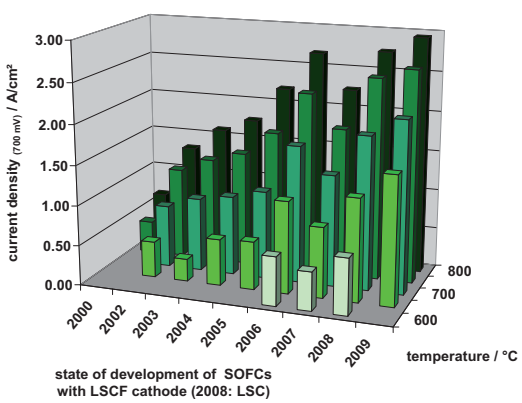
Pricipal inventor	PT	Descriptoin
J. Mergel	1.2334	Cooling unit for fuel cells

3.3 Key topic: solid oxide fuel cells

3.3.1 Objectives and fields of activity

Solid oxide fuel cells (SOFCs) generate electricity and can be operated not just with pure hydrogen but also with a number of other fuels including biogases and diesel reformate. This makes this type of fuel cell suitable for different stationary and mobile applications – for example, in the field of local energy production in single-family houses and multifamily dwellings or for industrial consumers, as well as in the area of mobile applications for on-board power supply in vehicles, ships and aircraft.

In the field of research and development, the "Electrochemistry of Solid Oxide Fuel Cells" working group tests stacks, as well as single cells, in order to investigate the impact of different operating conditions. The experimental facilities are equipped in such a manner that a number of fuel gas compositions can be used – from pure hydrogen to biogases with impurities such as hydrogen cyanide or hydrogen sulfide. In addition, special test facilities are being developed and built to allow the interaction between different stack components to be investigated. An example of this is the interaction between the metallic interconnect and the glass or metal sealant in different fuel cell atmospheres, whereby the electrically insulating function of the glass sealant is simultaneously monitored using resistance measurements. A similar setup also exists for the interaction between the contact layer or protective coating and the cathode material, whereby the conductivity is continuously measured. The interaction between interconnect materials (with and without a protective coating) and cells is also currently being studied, whereby the influence of metallic components on the cell performance can be selectively investigated.

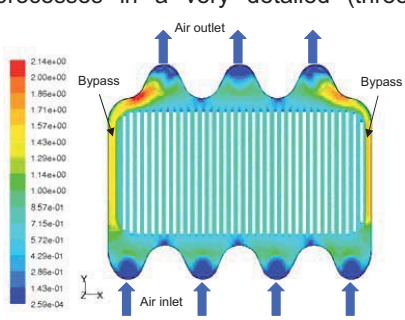


The different applications make different demands on the lifetime of a fuel cell. For stationary applications, a minimum lifetime of 5 years is essential. During this time, the fuel cell must not lose more than 10 % of its initial power. Long- term tests are carried out on both single

cells and stacks to fulfill this requirement, whereby performance is measured as a function of electrical load over time. In addition to the current load, the operating temperature and the fuel gas composition are also important parameters whose influence on performance is being investigated. Another topic related to development and optimization is the comparability of measurement results for different types of cells and the analysis of the influence of materials and/or fabrication techniques.

In the area of mobile applications, the demands made on stacks are much harder to satisfy than those in the area of stationary applications due to dynamic operation. Changes in load occur very often, thus causing the current density to vary considerably. In real systems, the temperature of the stack decreases when it is in standby mode and the stack must be brought to operating temperature as rapidly as possible when it is restarted. This places great demands on the materials used and on their thermomechanical stability. These processes are also investigated in stacks in order to characterize technologically interesting systems. The stack must also retain its power, for example losing no more than 10 % of its power after 100 cycles.

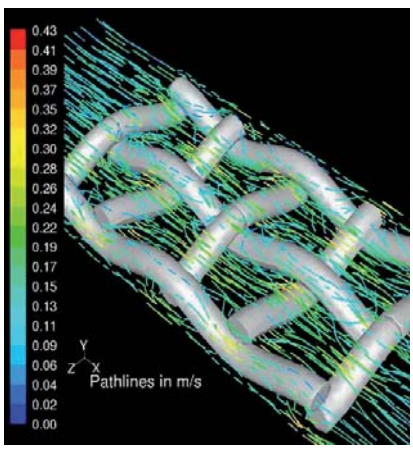
In addition to experimental studies, SOFC operation is also analyzed by mathematical modeling. The processes in the SOFC (charge, heat and mass transfer) are described by mathematical (partial differential) equations. The models can describe the structures and processes in a very detailed (three-dimensional) or very simplified (one-dimensional) manner. The latter models are much smaller and thus much easier to solve, which means that they can be used as one of the components in generic system simulations. Current, temperature and concentration distributions are determined by solving all model equations numerically (simulation calculations). The operating behavior of an SOFC can thus be predicted, providing optimized approaches to layout and design, which in turn accelerates development.



Modeling work is complemented in certain areas by experimental work, either to determine the input parameters for the calculations or to verify the calculation results. Thus, for example, mass transfer parameters in porous bodies (anode substrate, cathode layer) are selectively determined by diffusion and permeation measurements, which are then incorporated into simulation calculations. Moreover, in special measurement setups, the flow distribution is determined in the gas distribution channels inside the cell by pressure loss and pressure distribution measurements. The measurement setup permits a simple and rapid variation of the manifolds, so that the geometry for homogeneous mass distribution can be optimized.

The Fuel Cell Process Engineering Group is involved in the layout, design, and construction of test setups and their components, as well as process engineering system analyses. The main fields of work are:

Testing of plant components: For specific boundary conditions coupled with operation at temperatures between 600 and 900 °C, the basic components of an SOFC system, such as a recuperative heat exchanger, pre-reformer or afterburner, are not commercially available. For this reason, test facilities are being set up to characterize third-party products as well as products developed internally and to test them in terms of their suitability. Development work is supported by the use of CFD to analyze the operation of the components, and suggestions for optimizing design and operation are also made.



Testing and optimizing concepts for controlling and regulating SOFC systems: Fuel cells require complex plant and process engineering. In order to be able to reliably operate the plants, safely control the different operating modes and prevent damage to the plant and fuel cells, special control and regulating concepts are required. These are worked out on the basis of experience acquired testing cells and stacks, and tested and further developed in the existing plants.

Development and construction of plants: In order to demonstrate the feasibility of the technology and test the interplay of all components, an SOFC demonstration plant is being developed and built, which will be run on natural gas and should achieve an electric power of 20 kW.

Calculation and evaluation of plant concepts: Based on experimental experience, steady-state and dynamic simulation calculations are carried out using different tools, with which different plant concepts can be evaluated and individual plant components designed.

3.3.2 Important results

3.3.2.1 Cell and stack development

Over the last few years, the focus in the field of SOFC cell and stack development was on improving performance. Today, the performance of cells is very good thanks to targeted modification of materials and (micro)structures. The same goal also applied to stack development. In addition to testing a new type of interconnect steel and newly developed cathodes, measurements were conducted to optimize the thickness of the cathode contact layer, the contact geometry between cathode and interconnect, and to investigate whether a protective coating was necessary on the cathode side of the interconnect. The second priority lay on investigating the lifetime of cells and stacks. These experiments on stacks were mainly carried out within the framework of the Real-SOFC EU project and the results will be presented in the section on selected R&D projects (see Chapter 4.2).

Activities related to the lifetime of single cells concentrate mainly on the influence of impurities on the electrocatalytic properties of cells. These impurities can originate from the materials used in the system or from external sources such as gas impurities.

Chromium poisoning of the cathode

It has been known for some time that the presence of chromium species has a negative influence on the performance of the air electrode. Controversial discussions on different mechanisms of this poisoning can be found in the literature. Due to the unavoidable use of steels that develop chromium oxide in the stack and the system, preventing this poisoning is one of the most important objectives. This process must therefore be understood in detail. As part of a cooperation between IEF-1 and IEF-3, electrochemical measurements are performed on single cells in which steels containing chromium are purposely placed in the vicinity of the air electrode. By varying the process parameters, such as current density and duration of exposure, the quantity of chromium can be varied. The electrochemical measurements showed different reductions in the performance of the cells. By analyzing the cathodes using different methods, we attempted to determine the amount of chromium deposited (in oxides) as well as the distribution of chromium in the cathode. This information was then correlated with the electrochemical data and results of measurements to determine the rate of chromium evaporation in order to get a clear picture of the poisoning process.

Initial electrochemical measurements revealed that steels containing chromium have a significant influence on cell performance. Fig. 68 shows the behavior of the cell voltages of two identical anode substrate cells with LSM cathodes as a function of time. One of the cells was operated without any steel containing chromium in the system. This cell only exhibited a small decrease in performance over the total operating time. The second cell was operated in the presence of steel containing chromium and shows a clear decrease in cell voltage over the total operating time.

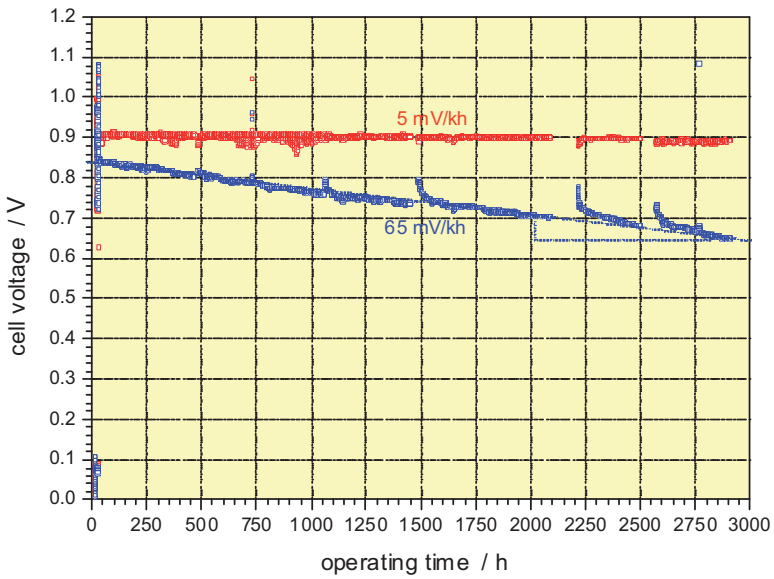


Fig. 68: **Cell voltage as a function of operating time for two anode substrate cells operated at 0.3 A/cm² and 800 °C with hydrogen: (red) without and (blue) with steel containing chromium in the cathode gas chamber**

Wet-chemical analysis was used to determine the total amount of chromium incorporated into the cathode layer. A tendency to increase was only found when the cell was exposed for less than 1,000 hours. For longer exposure times, the amount of chromium incorporated only increased very slightly.

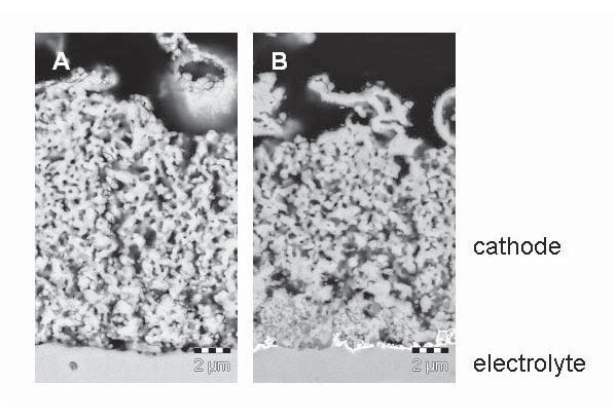


Fig. 69: **Electron micrograph of the interface between cathode and electrolyte after (A) 250 hours and (B) 3,000 hours of operation at 800 °C with steel containing chromium in the cathode gas chamber**

Fig. 69 shows electron micrographs of cross sections of cells at the cathode-electrolyte interface for different exposure times. When exposure time was increased, a clear increase in impurity phases was also observed, which strongly reduced the porosity of the cathode. Furthermore, the microstructure of the starting materials clearly changed at the interface. The thickness of the layer in which these impurity phases occurred appeared to grow with the exposure time. These impurity phases are composed of a chromium-manganese spinel.

Impurities in the fuel

When the fuel used is not pure hydrogen, the presence of impurities is very difficult to avoid. Fuels with a biogenic origin, in particular, are heavily loaded. The main components are sulfides, cyanides, halogenides, borides and aromatics as well as unsaturated hydrocarbons. In order to test the influence that some of these fuel impurities have on the electrochemical properties of single cells, a test rig was modified to allow these impurities to be fed into the fuel flow in the ppm range.

One component was chosen to represent each of the various different types of impurities. To date, measurements have been performed for hydrogen sulfide, hydrogen cyanide and toluene. Concentrations of up to 100 ppm for toluene and 20 ppm for hydrogen cyanide were found to have no influence on cell performance or degradation behavior (Fig. 70).

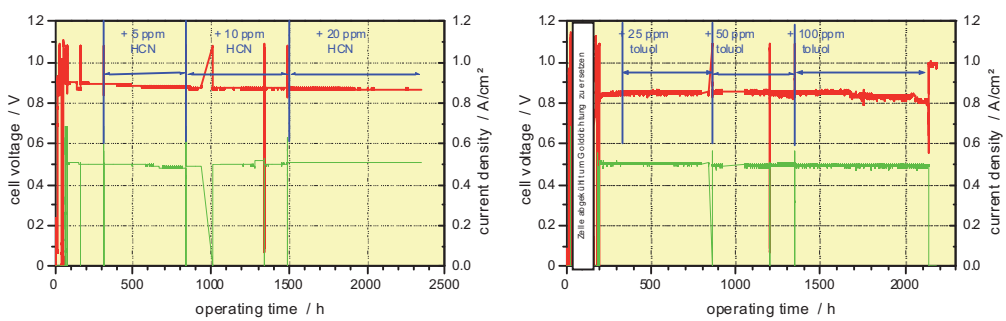


Fig. 70: Cell voltage as a function of operating time for an anode substrate cell operated at 0.5 A/cm² and 800 °C with hydrogen: (left) addition of HCN of up to 20 ppm; (right) addition of toluene of up to 100 ppm

For hydrogen sulfide, the situation is very different. Concentrations of 30 ppm in hydrogen cause a significant decrease in cell performance when added (see Fig. 71). The cells then operate with a degradation rate of approximately 6 % in 1,000 hours, which is at least six times higher than with pure hydrogen. This increase in the degradation rate was observed for H_2S concentrations greater than 20 ppm. The degradation rate is however not proportional to the H_2S concentration. The experiment shown in Fig. 71A allows the conclusion to be drawn that it is possible to reverse the reduction in performance by stopping the addition of hydrogen sulfide. The experiment shown in Fig. 71B is very different. Under nominally identical conditions with the same cells, catastrophic failure of the cell occurs after a certain time. This is caused by a conversion of nickel to nickel sulfite in the anode substrate (Fig. 72).

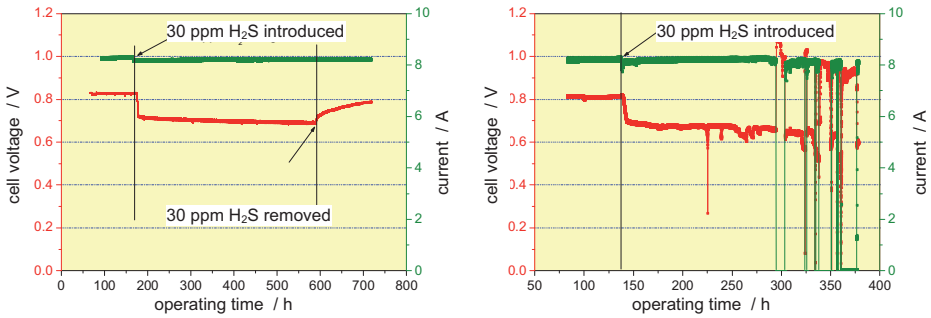


Fig. 71: **Cell voltage as a function of operating time for an anode substrate cell operated at 0.5 A/cm² and 800 °C with hydrogen with the addition of 30 ppm hydrogen sulfide**

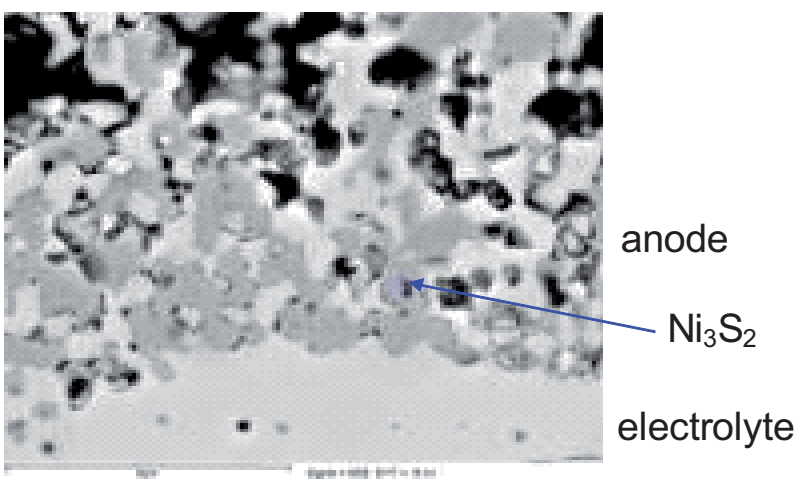


Fig. 72: **Electron micrograph of the interface between electrolyte and anode after operation with fuel containing hydrogen sulfide. The EDX analysis of the gray particles in the image revealed a chemical composition of Ni_3S_2. The interface contains almost no more free nickel**

Contact layer thickness

One of the problems associated with assembling and operating stacks was the lack of reproducibility of cell performance in stacks, both between different stacks as well as between cells within a stack. A measurement series compared stacks with cathode contact layers of different thicknesses. Until this point, the standard contact layer thickness was ~100 µm. Three stacks were assembled differing only in the thickness of their layers: 50 µm, 100 µm and 150 µm, respectively. Fig. 73 shows the current density-voltage curves for the cells in the three stacks. The results demonstrate that the performance of the individual levels is easier to reproduce with increasing contact layer thickness. These findings were

incorporated into stack assembly and have contributed to improved reproducibility of the electrochemical performance of stacks.

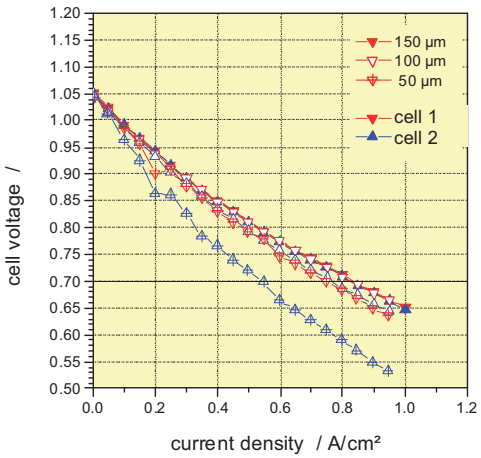


Fig. 73: Current density-voltage curves for three stacks with cathode contact layers of different thicknesses (50, 100 and 150 µm) operated at 800 °C with hydrogen

Creep-resistant interconnector steel

Within the framework of work aiming to improve the mechanical properties of the high-temperature-resistant steel used, a new variety of CroFer22APU with improved creep resistance (CroFer22H) was developed at IEF-2. In order to determine whether the changes in the composition of the steel have an impact on the electrochemical performance and the degradation behavior of stacks, a number of stacks with interconnect plates made of CroFer22H were assembled and tested. No significant differences were observed in electrochemical behavior for 1,500 hours of operation compared to stacks made of CroFer22APU, which were tested under the same conditions.

High-performance cathodes

Improvements in the electrochemical performance of stacks by using lanthanum-strontium-ferrite cobaltite (LSFC) cathodes led to a significant improvement in the electrochemical performance of stacks. These increases allow the operating temperature to be decreased by 100 °C while retaining the same stack performance. When LSFC cathodes are used, however, it is essential that a barrier layer of gadolinium-doped ceria (CGO) be applied between the YSZ electrolyte and the LSFC cathode in order to prevent a chemical reaction between YSZ and LSFC. The structure of this thin layer has a significant impact on the performance level and stability of the cells. Cells with barrier layers fabricated by means of physical vapor deposition (PVD) exhibited better performance levels in single-cell measurement than cells in which this layer was fabricated by means of screen printing. However, in stacks that were otherwise identical, no difference was ascertained between these cells for which CGO barrier layers were fabricated in different ways. The reason for this is the relatively high resistance of the contacts in the stack in relation to a very low cell

resistance. The contact resistances determine to a large extent the performance of the stack when cells with LSFC cathodes are incorporated. This result shows that there is room for improvement in terms of the contact situation in the stack. This will be improved by modifying the materials and adapting the geometry.

Protective coating

In order to prevent the evaporation of chromium species from steels containing chromium as far as possible, a protective coating is applied to the interconnect plates. This manganese oxide layer helps a chromium-manganese spinel layer to form on the steel. In order to test the effectiveness of this layer, two stacks of identical design were used except that one stack contained no protective coating. Fig. 74 shows the distribution of cell voltages for both of these stacks.

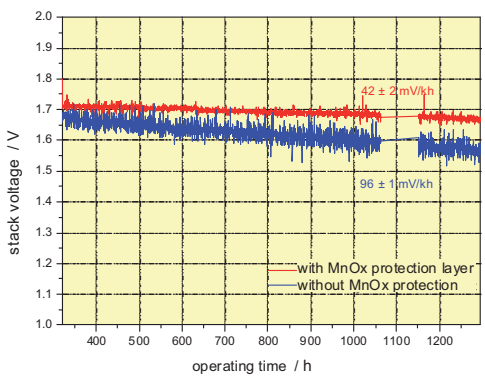


Fig. 74: Cell voltages as a function of operating time for two stacks operated at 800 °C and 0.5 A/cm² with hydrogen: (red) with and (blue) without a manganese oxide protective coating on the interconnect plates

The absence of the manganese oxide protective coating has a clear impact on the degradation rate of the stack. With a mean value of 96 mV over 1,000 hours, it is twice as high as for the stack with a manganese oxide protective coating.

3.3.2.2 System development and verification

Chromium evaporation measurements

As part of the BMWi-funded project known as ENSA (Development of SOFC APUs), a number of tests were performed on heat exchangers on behalf of one of the companies involved.

It is widely known that chromium, which evaporates in the SOFC stack from the interconnects, is incorporated into the cathode and can lead to increased degradation here. As the materials in the peripherals also contain chromium, in particular the air preheater, it is important to determine how much chromium can escape from these sources and enter the stack. Chromium evaporation measurements were therefore carried out on high-temperature

exhaust-gas heat exchangers in steady-state and cyclic operation under the following boundary conditions:

In order to determine the chromium evaporation rate, a small partial flow (approx. 0.1 to 0.2 %) is siphoned near the heat exchanger outlet (after an inert tube section) through a small glass tube in which the chromium condenses out during cooling. The diverted flow rate is measured and used to extrapolate the total volume. The volume of chromium (and some other metals) that was condensed out and captured in this small glass tube and the connected cooler are subsequently rinsed with acid and analyzed. The configuration of the sampling point for the chromium evaporation measurements is shown in Fig. 75.

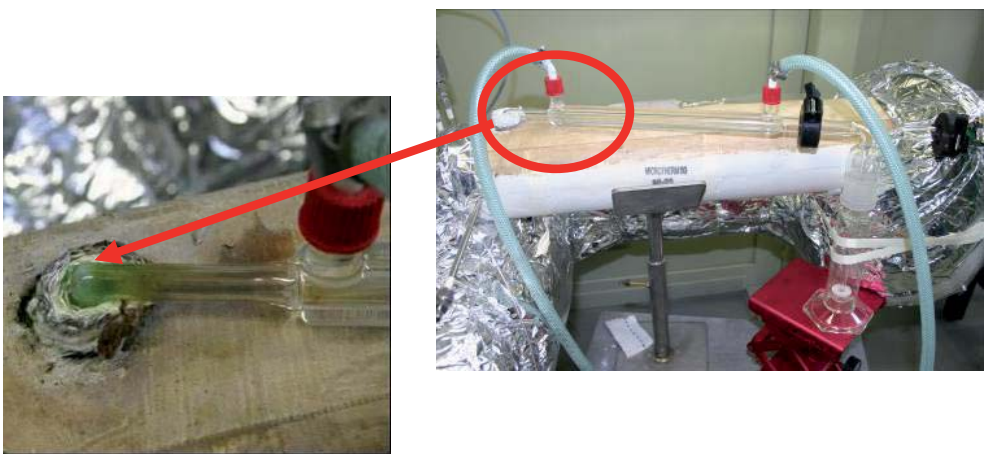


Fig. 75: Configuration of the sampling point for the chromium evaporation measurements

It is assumed that the chromium concentrations in the main flow and sample flow are the same, and that the total chromium volume siphoned into the collecting tube precipitates on the inner walls of the collecting tube and the downstream gas washing bottle.

Sampling is conducted over 75 cycles for cyclic tests, and over approx. 50 hours for steady-state tests. In a 1,000-hour experiment, sampling is performed six to seven times. In preliminary tests, it was ascertained that lengthy sampling (approx. 200 hours) led to the formation of a stable chromium coating, which was not dissolved by subsequent acid rinsing.

Two steady-state tests were then performed, each with a duration of 1,000 hours. In these tests, one uncoated and one coated heat exchanger were tested. The results of the chemical analysis of the samples were used to determine the amount of chromium in the complete cold outlet flow. The area below the curves was integrated for the captured chromium and used to determine the amount of chromium discharged over time (always in relation to the total air volume flowing through; see Fig. 76). It can be seen that by coating the heat exchanger, the discharge of chromium can be reduced by a factor of approx. 20.

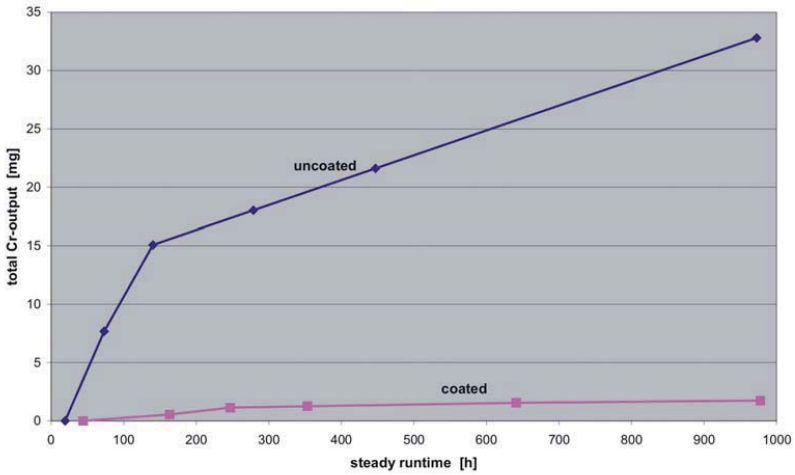


Fig. 76: Comparison of two heat exchangers: cumulative Cr volume in the cold outlet flow

Following this, cyclic tests were performed (see description in the next chapter). In these tests, once again one uncoated and one coated heat exchanger were tested. At the beginning of the test, the maximum chromium evaporation was observed for the uncoated heat exchanger and the minimum chromium evaporation for the coated heat exchanger. Between the 350th and 750th hour of operation, similar chromium evaporation was measured in both heat exchangers. From the 750th hour of operation onwards, the evaporation in the coated heat exchanger was slightly higher than in the uncoated heat exchanger. In cyclic operation, the coating of the heat exchanger does not have as significant an effect as it does in steady-state operation. This can be explained by damage to the coating as a result of cycling. In relation to the cumulative chromium volume, chromium evaporation with the coated heat exchanger is initially 25 times smaller. This factor decreases to 1.7 during the course of the test.

Thermomechanical analyses

For use as an APU in vehicles, the system must exhibit very good dynamics. In order to test how suitable the heat exchanger is, temperature cycling tests were conducted under the following conditions:

- two exhaust-gas heat exchangers were tested in parallel in each case
- 200 temperature cycles were completed with heating cycles lasting approx. 4 min and cooling cycles approx. 60 min
- the hot-gas temperature was at least 900 °C
- the cold gas was heated to 700 °C in 4 minutes

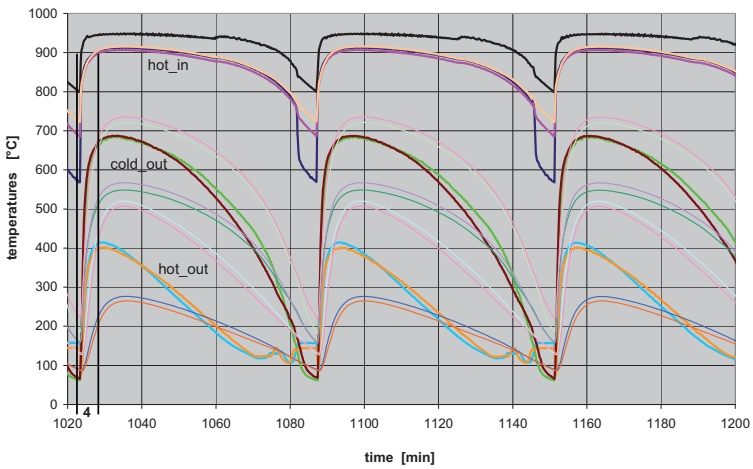


Fig. 77: Temperature curves for fast thermal cycling

A total of 21 pairs of heat exchangers were tested. The test for each pair of heat exchangers consisted of a cyclic part (four runs with 50 cycles each) and a steady-state part. The temperature curves during cycling are shown in Fig. 77 as an example

Charcterization of functionality

In the Large SOFC EU project (development of plants with a power of 50 kW or greater), plant components are being developed, tested and characterized in a working package.

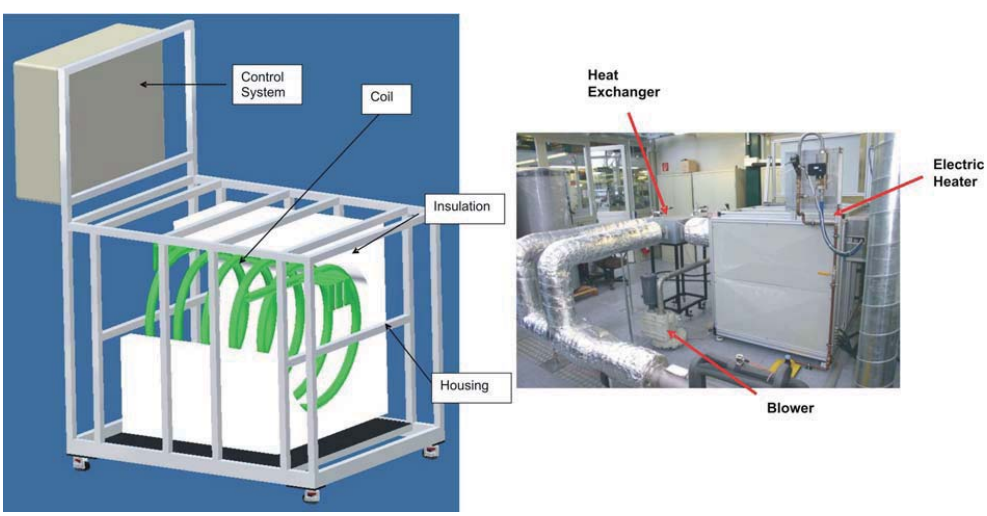


Fig. 78: Heat exchanger test rig 900°C/200 m_N^3/h – schematic and completed assembly

One of the objectives is to test heat exchangers at temperatures of up to 900 °C at an air flow rate of 200 m_N^3/h. As none of our partners had access to such facilities, a test rig had to be developed and constructed. Using the electric ovens in existing heat exchanger test rigs as a basis, the new air heater was also to consist of an electrically heated pipe coil. However, the heating power had to be increased from 15 kW_{el} to 43 kW_{el}. An illustration of the individual parts as well as a photo of the assembled test rig can be seen in Fig. 78. The LabView software was used to monitor the test rig and to record data. For the test rig as a whole, a failure mode and effects analysis (FMEA) was performed as part of CE certification. Before assembly, a leak test was performed on the heat exchanger delivered by our project partner Wärtsilä. As no leak was determined, the tests were begun.Natural gas reformer

For the integrated module in the 20-kW plant, special planar reformers were developed and fabricated. Despite problems with tightness (see IEF-3 Report 2007), work began on system tests with two reformers. At the same time, the design was analyzed and optimized and the fabrication technique was further improved. Applying the solder using a solder foil instead of screen printing was qualified in a number of preliminary tests. Using this technique, four newly fabricated reformers were successfully soldered for the 20-kW system. This reformer also has a modified plate design.

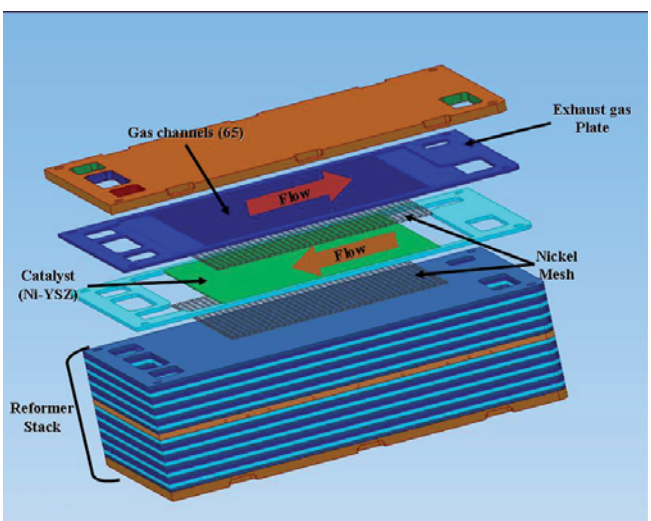


Fig. 79: Setup plate reformer

The configuration of the plate reformer, as shown in Fig. 79, was analyzed using CFD (from the Fluent company) in order to further optimize the system. A distribution analysis of the flow velocity revealed good homogeneous distribution with deviations < 10 % (Fig. 80).

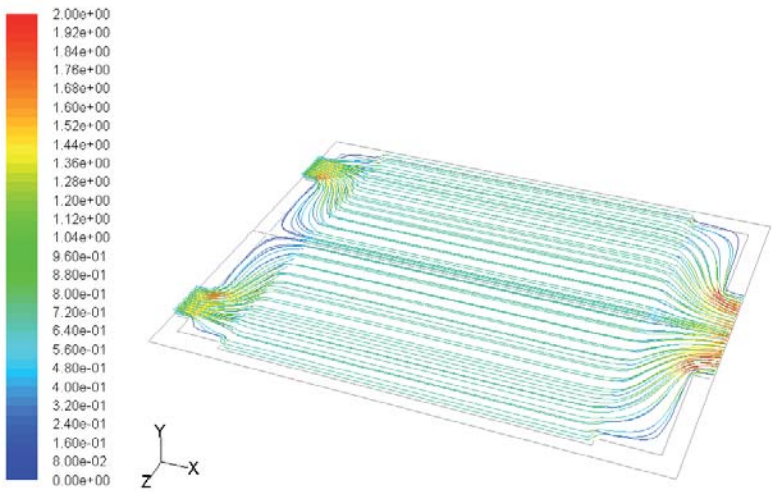


Fig. 80: Plate reformer: calculation of the distribution of flow velocity [m/s]

The next step involved analyzing the reaction rates determined from the measurements and the resulting changes in gas composition. This behavior was reproduced by CFD calculations in order to gain a reliable basis for further design optimizations.

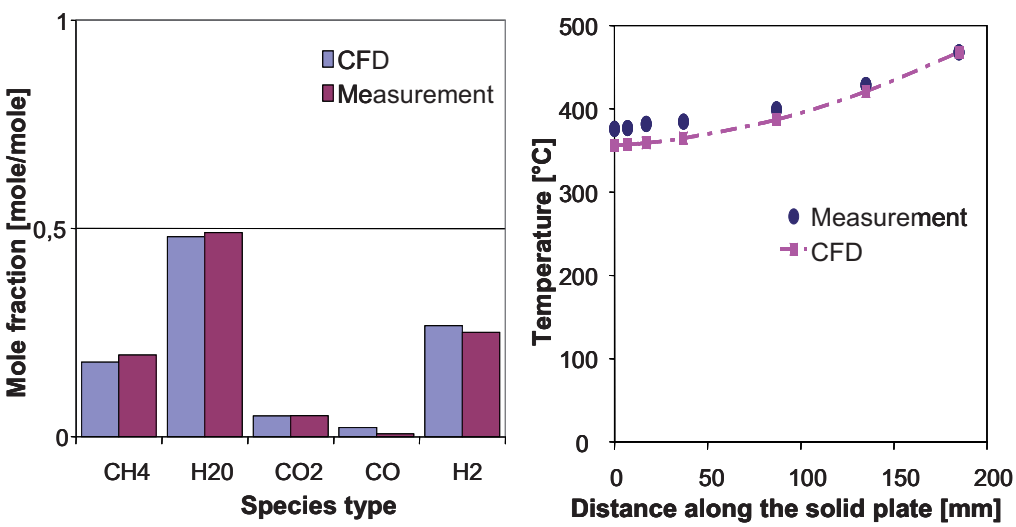


Fig. 81: Reformer gas composition at the outlet and temperature curve from inlet to outlet

As reforming occurs in the prereformer at relatively low temperatures (400 to 600 °C), the reforming kinetics which are used for SOFC stacks are not accurate enough. Initial modifications showed good agreement with the leakage composition but had slight deviation

in temperature curve (Fig. 81). It is planned to implement kinetics for low-temperatures next as determined a number of years ago at IEF-3 within the scope of a PhD thesis.

20-kW SOFC system

The first tests in dummy operation had to be discontinued prematurely because the heating plates used to heat the system failed after a short time (see IEF-3 Report 2007). A new heating plate design was developed in which the heating wires were replaced with cartridge heaters. A preliminary test with the new heating plate design with a heating plate temperature of 800 °C for 1,000 operating hours, and subsequently at 850 °C for 850 operating hours proceeded without failure. Although the insulation resistance decreased to 25 kOhm as the test progressed, this did not represent an obstacle to operation in the system.

The damaged heating plates in the 20-kW system were subsequently replaced with the new plates and the dummy tests continued. In test 01, a total of 4 heating plates were used (2 dummy plates, 2 afterburners) and heated with a heating rate of 4 K/min. In test 02, the same heating plates were heated with a heating rate of 2 K/min. When the stack dummy temperature of 700 °C was reached in both cases the heating was turned off. At a heating rate of 4 K/min, a stack dummy temperature of 700 °C was reached after approx. 4.5 hours. The same temperature was achieved after approx. 6.5 hours at a heating rate of 2 K/min. The test reveals that it is possible to heat the integrated module up to operating temperature with the heating plates used. Other tests were conducted with different heating rates and/or modified gas flows. Following the heating tests, evaporation tests were conducted in steady-state dummy operation. After these initial dummy tests, the modules were disassembled and the reformer was replaced with the newly fabricated tighter components described above. All other components were tested for tightness and flatness. No changes were determined in relation to the original state.

After the modules had been reassembled, further heating tests were performed, as were experiments involving feeding natural gas into the system in order to test the ignition performance of the afterburner. As can be seen in Fig. 82, the temperatures of afterburner, air preheater and dummy at a heating power of twice 4 kW increased with little offset, while the prereformer, which is furthest away from the heating plates heated up much more slowly. The latter is desired as the operating temperature is lowest here. At 600 °C, hydrogen begins to ignite in the afterburner because the hydrogen concentration in the exhaust gas decreases (curve % LEL (lower explosion limit) in exhaust gas). At 700 °C, no more hydrogen was measured in the exhaust gas. At an afterburner temperature of 800 °C, water was supplied in order to generate steam for reforming. A short time later, natural gas was fed in, which led to a rapid increase in the temperature of the afterburner. An increase in air volume counteracts this. For reduced natural gas volumes, the system can be held at operating temperature when it is running idle. These tests will be continued in order to make it possible to heat the system as fast as possible by feeding in natural gas earlier.

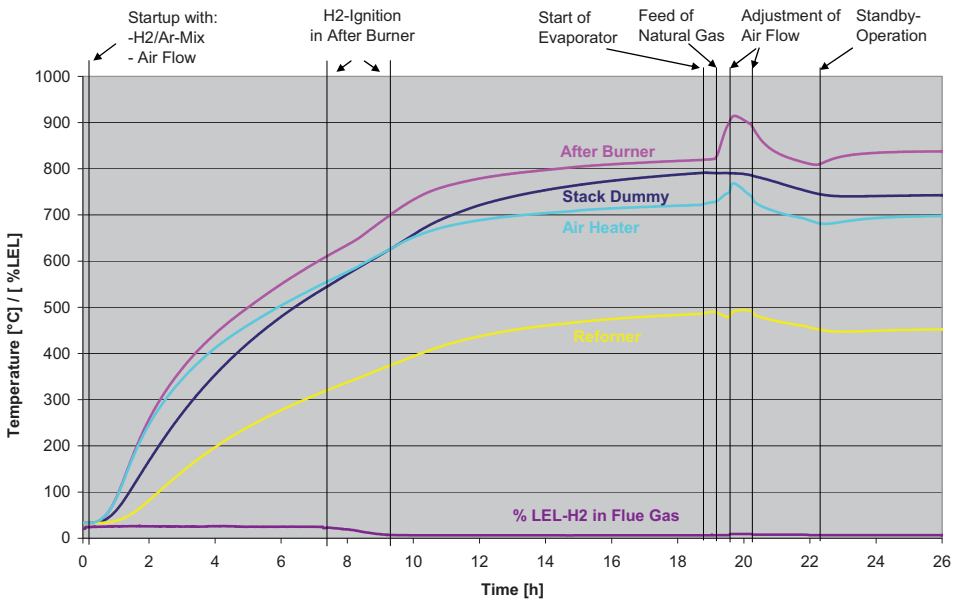


Fig. 82: Dummy operation – behavior during heating

3.3.2.3 Modeling and simulation

The “GenFC” Eu project aimed to significantly accelerate the development of fuel cell technology. This task was tackled from two angles at the same time.

On the one hand, a number of fuel cell models were developed within the project providing solutions to current problems associated with the technology in use today. The breadth of topics ranges from simulating mass transfer (taking different liquid and gaseous components into account) on the channel level of a fuel cell to describing entire building complexes with integrated combined generation of heat and power.

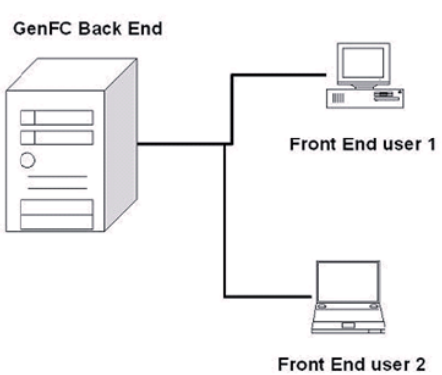


Fig. 83: Front end and back end configuration of the GenFC software

On the other hand, a structured software framework was created for fuel cell simulation. This framework aims to generically support modeling activities for the whole range of fuel cell simulations. Furthermore, data from simulations and measurements can be saved, processed and compared in this system. The GenFC framework consists of two main components (Fig. 83): the database server and the front end. Activities in IEF-3 related to the GenFC project focused on developing the front end.

The function of the front end is to

- provide the user with a graphical interface for data management, and
- provide a simple test environment for stand-alone models, which can easily be expanded by programmers.

The function of the back end is to

- provide the data requested by the front end,
- save all simulation and measurement data in the database in a coherent and organized manner,
- provide multiple users with simultaneous secure access to the database.

Fig. 84 shows a screen shot of the graphical interface developed in this institute. Hidden behind the relatively simple operating elements are much more complicated concepts, such as generic interfaces and the data model with its own object manager.

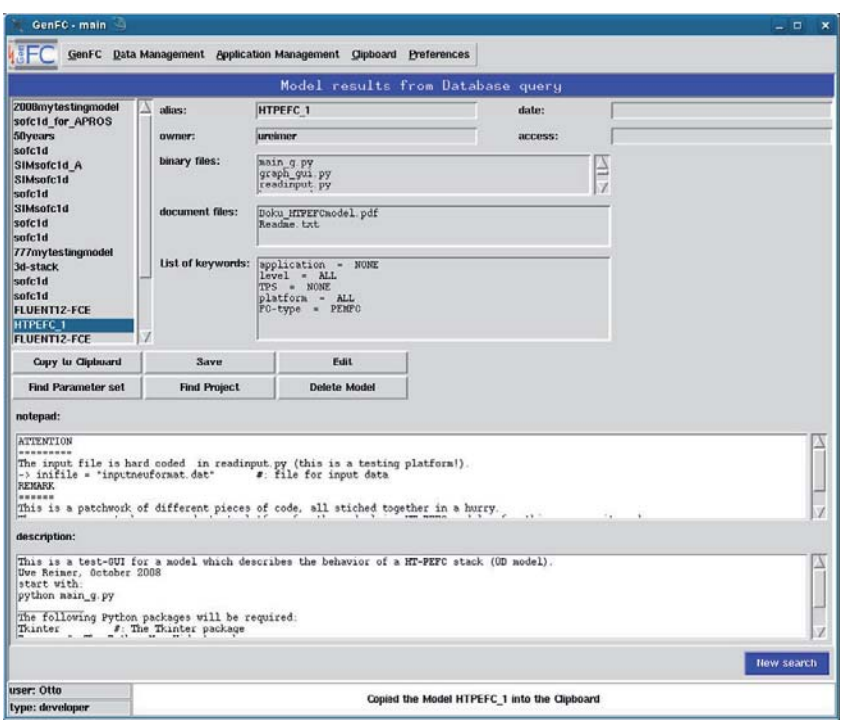


Fig. 84: Graphical user interface for database queries of models

The conclusion of the “GenFC” project saw a cornerstone being laid with the basic version of the software – by generically expanding it, this basic version can be adapted to deal with current issues. This will be done mainly in a series of bachelor and diploma dissertations. Work began on the first diploma dissertation on this topic in October 2008.

3.3.3 Staff members and fields of activity

Name	Tel. (+49 2461-61-) E-mail address	Field of activity
Dr. L.G.J. de Haart	6699 l.g.j.de.haart@fz-juelich.de	Head of SOFC Electrochemistry and Simulation
Ms. S. Berns	6697 s.berns@fz-juelich	Software development, modeling
Prof. L. Blum	6709 l.blum@fz-juelich.de	Head of Fuel Cell Process Engineering
Dr. K. Cerny	5170 k.cerny@fz-juelich.de	Software development, modeling
P.H. David	4652 p.h.david@fz-juelich.de	Electrical engineering, measurement data recording and systems control
R. Deja	5291 r.deja@fz-juelich.de	System simulation, development and testing of SOFC system components
D. Froning	6676 d.froning@fz-juelich.de	Computer science, software engineering, modeling
Dr. V.A.C. Haanappel	4656 v.haanappel@fz-juelich.de	Chemical technology, (high-temperature) corrosion
Ms. A. Kind	3850 a.kind@fz-juelich.de	Software development, modeling
Ms. J. Kuhl	6697 j.kuhl@fz-juelich.de	Software development, modeling
Dr. M. Peksen	8732 m.peksen@fz-juelich.de	Testing and simulation of system components
Ro. Peters	4664 ro.peters@fz-juelich.de	Head of the SOFC Systems Technology Group, component development, plant design, construction and testing
Dr. M. Spiller	1573 m.spiller@fz-juelich.de	Head of the SOFC Simulation Physics Group, software development, CFD modeling

Dr. I.C. Vinke	6688 i.c.vinke@fz-juelich.de	Electrochemistry, solid-state ionics, high-temperature electrochemistry

3.3.4 Important publications

Important publications

Blum, L., Buchkremer, H.P., Gross, S., Gubner, A., Haart, L.G.J. de, Nabielek, H., Quadakkers, W.J., Reisgen, U., Smith, M.J., Steinberger-Wilckens, R., Steinbrech, R.W., Tietz, F., Vinke, I.C.

Solid Oxide Fuel Cell Development at Forschungszentrum Jülich

Fuel Cells 7 (2007) 204 – 210.

SOFC development work at Forschungszentrum Jülich is extensive, ranging from fundamental materials' design through to near-commercial prototype CHP systems. Considerable advances have been demonstrated in the past few years concerning the improvement of device performance. This was achieved by identifying performance degradation mechanisms and reducing or eliminating those problems, and in designing, developing and manufacturing core SOFC components. At the time of writing, a first fully-integrated SOFC combined heat and power generation prototype system is awaiting completion. Forschungszentrum Jülich is involved in significant national and international programs and coordinates major international projects.

Blum, L., Buchkremer, H.P., Steinbrech, R.W., Haart, L.G.J. de, Reisgen, U., Steinberger-Wilckens, R.

Current Trends of SOFC Development at Forschungszentrum Juelich

8th European Solid Oxide Fuel Cell Forum, 30.06 – 04.07.2008, Lucerne, Switzerland: CD ROM B306.

Throughout the past 12 years, the SOFC group at Forschungszentrum Jülich (Jülich) has assembled and tested more than 300 SOFC stacks, rated between 100 W and 15 kW. Stacks are being tested systematically for the influence of materials and operating conditions on stack performance and durability. In parallel, in-depth analysis is being performed on degradation phenomena in order to obtain the information necessary to avoid the gradual loss of power. A large number of stacks with a rating of 100 W_{el} to 5 kW_{el} have been delivered to partners within the Real SOFC project and other developers worldwide. They prove that SOFC stacks can be successfully assembled, tested and delivered. Light-weight stacks for the application of SOFC as auxiliary power units are being developed in the cassette design and they have been tested under severe conditions such as heating rates up to 25 K/min.
Laboratory systems with an electric power output of 1 and 20 kW are in preparation using the integrated stack concept that combines all elevated temperature balances of plant components and the stack itself into one single module. The assembly of the 20-kW system has been completed and dummy testing has commenced.
The development of high-performance cathode materials has resulted in high current densities up to 2.7 A/cm² at 0.7 V and 800 °C. One of the main objectives of research is the optimization of stack components in order to maintain this high power density when integrating the cells into stacks.

The use of the Jülich-developed ferritic steel CroFer22APU has resulted in reduced degradation rates of around 1 % per 1,000 hours over stack lifetimes of more than 6,000 hours at increased current densities of 500 mA/cm² at a reduced operating temperature of 700 °C. However, for stationary applications, less than 0.25 %/ 1,000 hours has to be achieved. Therefore, further improvements of the interfaces within the stacks are necessary.

Froning, D., Berns, S., Krötz, D., Reimer, U.

GenFC in the Role of Experimental Validation

8th European Solid Oxide Fuel Cell Forum, 30.06 – 04.07.2008, Lucerne, Switzerland: CD ROM A204.

Modeling plays a very important role in the development of fuel cells and fuel cell systems. Until today, many companies and research organizations have successfully developed their own simulation models. The development of fuel cells and fuel cell systems can not only be improved by simulation models but also by the flow of information – from the developer to the developer of models, or from the developer to the application engineers and experimenters. This process can be supported by the Generic Fuel Cell Modeling Environment (GenFC).
GenFC offers a database for storing all data in a defined way. Linking together models, parameter data and simulation results is supported by the structure of the database. It is vendor independent and neither restricted to a special type of fuel cell nor to simulation models applied to certain modeling frameworks. Furthermore, it supports different levels of fuel cell modeling. These include CFD simulations for detailed three-dimensional structural information and also more abstract behavior models which can simulate the behavior of fuel cells, fuel cell stacks or even fuel cell systems in less computing time – even hardware in the loop (HiL) experiments are candidates for the GenFC framework.
The project GenFC is an EC-funded project in the Sixth Framework Programme. Its motto is “To bring together the people and the information”. To support the information exchange between modelers, engineers and experimenters, a data model was developed to encourage the linking of information between all of these people using essential keywords and structural information. The GenFC software was designed as a client-server architecture. The server is a database management system supporting the data model mentioned above. A framework acts as a client allowing the organization of simulation models, their input data and simulation results in a comfortable way. Furthermore, experimental data can also be included in the information structure to enhance the integrity of the stored knowledge.
This paper provides an introduction to the data model and the basic concepts of the GenFC framework. The measured data on a 60-cell SOFC stack fabricated by Forschungszentrum Jülich is taken as an example to show how the GenFC software can help validate SOFC simulation models and document them. For this purpose, two different SOFC simulation models – a CFD-based structural model and an ODE-based behavior model – are taken to show the connection between the two simulation models, the experimental data, and the documentation in the network of stored information in the GenFC database.

Froning, D., Blum, L., Gubner, A., Haart, L.G.J. de, Spiller, M., Stolten, D.

Experiences with a CFD Based Two Stage SOFC Stack Modeling Concept and its Application

ECS Transactions – Solid Oxide Fuel Cells 7 (2007) 1831 – 1840.

The parallel development of kW-range SOFC stacks and their systems at Forschungszentrum Jülich requires distinguished modeling capabilities using validated SOFC models targeting the three-dimensional stack structure itself as well

as the entire system. For the full three-dimensional (3D) geometric resolution of a stack, computational fluid dynamics (CFD) models are used, whereas a one-dimensional (1D) behavior model based on ordinary differential equations (ODE) covers the system modeling requirements.
The CFD model uses advanced data structures to reduce the computing time significantly. However, computing times in the range of seconds or below required by system modeling feature only in the 1D model.
Both SOFC models are based on the same physical equations for electrochemical conversion and internal methane reforming.
The application of these models is shown in practice, focusing on choosing the right model for an application. We also describe how both models were validated against each other and against experiments.

Haart, L.G.J. de, Mougin, J., Posdziech, O., Kiviaho, J., Menzler, N.H.

Stack Degradation in Dependence of Operation Parameters; the Real-SOFC Sensitivity Analysis

8th European Solid Oxide Fuel Cell Forum, 30.06 – 04.07.2008, Lucerne, Switzerland: CD ROM B1002.

The EU Integrated Project Real SOFC aims at improving our understanding of degradation in SOFC stacks and extending the durability of planar SOFC stacks to degradation rates suitable for stationary application. As part of the Real SOFC project, three series of SOFC stacks each with 2 or 4 planar anode-supported cells were operated for durations of up to 3000 h (and longer) under varying fuel and electrical load conditions. The durability tests of these short stacks were conducted galvanostatically at 800 and 700 °C in dependence on current density (0.3, 0.5 and 0.7 A/cm²), fuel composition (hydrogen: H_2 + 3… 10 % H_2O or methane: CH_4/H_2O (S/C=2) and fuel utilization (8, 40, 60 or 75 %). A pronounced difference in degradation behavior was observed between the stacks operated at different current densities. The degradation behavior was, however, not influenced by the choice of fuel (hydrogen or methane) and was hardly influenced by the fuel utilization.
The lowest degradation rates of about 20 mΩ•cm²/kh were determined in the tests on a short stack with cells with LSM cathodes operated at 800 °C and a current density of 0.3 A/cm² and in tests on a short stack with cells with LSCF cathodes operated at 700 °C and a current density of 0.5 A/cm².
Post-test characterization of the cathode with respect to chromium poisoning was performed on cells from several stacks. No clear relationship was established between the degradation rate of the stack and amount of Cr incorporated in the cathode. The major difference was a change in the microstructure of the cathode in the region near the electrolyte interface; in the stacks operated at lower current densities, the structurally changed zone was clearly thinner than in those stacks operated at higher currents.

Haanappel, V.A.C., Batfalsky, P., Gross, S.M., Haart, L.G.J. de, Malzbender, J., Menzler, N.H., Shemet, V., Steinbrech, R.W., Vinke, I.C.

A Comparative Study Between Resistance Measurements in Model Experiments and Solid Oxide Fuel Cell Stack Performance Tests

Journal of Fuel Cell Science and Technology 4 (2007) 11 – 18.

Several combinations of glass-ceramic and steel compositions with excellent chemical and physical properties have been tested in the past in SOFC stacks, but there have also been some combinations exhibiting pronounced chemical interactions causing severe stack degradation. Parallel to the examination of these degradation and short-circuiting phenomena in stack tests, recently less complex model

experiments have been developed to study the interaction of glass-ceramic sealants and interconnect steels. The sealants and steels were tested in the model experiments at operation temperature using a dual air-hydrogen atmosphere similar to stack conditions.
The present work compares electrochemical performance under constant current load of SOFC stack tests with the resistance changes in model experiments. In addition, microstructural results of post-operation inspection of various sealant-steel combinations are presented.
The model experiments show that under the chosen experimental conditions distinct changes in the specific resistance of the specimens correlate well with the changes in the electrochemical performance of SOFC stacks, indicating that this method can be considered as an excellent comparative method to provide useful information on the physical and chemical interactions between glass-ceramic sealants and ferritic steels.

Haanappel, V.A.C., Smith, M.J.

Quality Assurance and Solid Oxide Fuel Cell Testing at Forschungszentrum Juelich

Journal of Fuel Cell Science and Technology 4 (2007) 11 – 18.

Standardization of fuel cell testing to allow comparisons presents one of the major challenges facing the fuel cell community. This becomes more critical when there is a need to make commercial decisions on the direction of the technology. One part of the development towards such standardization is the formalization of what measurements are made and how they are made, including the control of external and environmental parameters.
This presentation details some of the elements of the standardized measuring system in place at Forschungszentrum Jülich and explains some of the rationale behind this system. The established measurement system adopts many of the principles employed by generic international quality assurance standards and commercial organizations. An analysis of the testing process identifies critical control points, e.g. those parameters that must be controlled to ensure internally consistent test results and repeatability. The Forschungszentrum Jülich solid oxide fuel cell (SOFC) testing process is illustrated by means of a flow chart. This chart details critical control points and shows how the parameter measurements are documented in systematic fashion. Specific examples are given of SOFC test data to illustrate how Forschungszentrum Jülich determined some of the critical control parameter values used in our testing. Those included are: the effects of Ni-cermet reduction temperature; the effect of the chosen time intervals between individual I-V measurement points; and finally the effect of the hydrogen flow rate. Standardization within the SOFC community can prove a contentious issue, but whatever standard test parameters are finally chosen by the community, to allow comparison of SOFC options, organizations will must introduce a well-designed, controlled and formalized measurement system. We have found that adopting a generic QA systems approach has been successful internally and recommend this option to other organizations.

Haanappel, V.A.C., Smith, M.J.

A Review of Standardising SOFC Measurement and Quality Assurance at FZJ

Journal of Power Sources 171 (2007) 169 – 178.

The need for standardization or quality assurance (QA) is argued for citing extant problems with consistency, repeatability and reliability of data. A review of the cell testing procedure or QA system used at Forschungszentrum Jülich is provided, including an outline of how the Forschungszentrum Jülich system was developed. This is put in the context of more extensive QA systems following the outlines of the ISO 9000 series standards. Examples are used to illustrate how and why a number of standard cell test parameters was adopted. It was found that pre-normative research

used to define testing parameters led to an improvement in cell performance generally. Therefore, it is recommended that other solid oxide fuel cell (SOFC) labs develop standardization in testing and QA systems to maintain and improve their measurement processes.

Haanappel, V.A.C., Röwekamp, B., Tropartz, C., Wesemeyer, H., Haart, L.G.J. de

Long-Term Endurance Tests of Single Cells under Various SOFC Operating Conditions

8th European Solid Oxide Fuel Cell Forum, 30.06 – 04.07.2008, Lucerne, Switzerland: CD ROM B0906.

From the mid 1990s onwards, Forschungszentrum Jülich has accelerated development work on, and the testing of, solid oxide fuel cells (SOFCs) based on an anode-supported cell (ASC) concept. The main targets in this research and development (R&D) work, aside from improving the specific power output, is to increase the durability of cells under a variety of typical SOFC application operational conditions.
In this paper, an overview is given of results from long-term endurance tests of a range of these ASC cells. Utilizing the same anode substrate, the cathode compositions are: $L_{a0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_3$ (LSCF) and $La_{0.65}Sr_{0.3}MnO_3$ (LSM). Results are discussed with respect to the influence of cathode composition, current density, operating temperature and fuel utilization, and we look at how these affect performance degradation rates.
In the case where degradation rates are described as voltage loss per kilo-hour (mV/kh) at constant current loading; the lowest performance degradation rates were observed with LSCF cathode cells ($Ce_{0.8}Gd_{0.2}O_2$ (CGO) physical vapor deposited: 3 – 5 µm thickness) tested at 750 °C under a current load of 0.5 A/cm². Increased current loading and lowered operational temperatures both resulted in higher performance degradation rates. No significant effect was observed as a result of varying the fuel utilization rate (u_F). It was found however that mV/kh is not the most useful measure of performance fade, and that changes in the area specific resistance (ASR) under pre-defined experimental conditions over time provide a better description for comparative purposes. The calculation of these ASR values however requires the periodic collection of current–voltage (IV) curve data during the long-term measurements, although it can be obtained by approximation from the absolute voltage drop over time by dividing by current density.

Haanappel, V.A.C., Mai, A., Uhlenbruck, S., Tietz, F.

Characterisation of Anode-Supported Solid Oxide Fuel Cells with PSCF Cathode

Journal of Fuel Cell Science and Technology 6 (2009) 011007-1 – 011007-6.

A systematic study was initiated of anode-supported single cells with $Pr_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ (PSCF) cathode. These solid oxide fuel cells (SOFCs) were characterized by electrochemical and diffusion and permeation measurements. In particular, the influence of various sintering temperatures of the cathode and of various types of $Ce_{0.8}Gd_{0.2}O_{2-\delta}$ (CGO) interlayer was investigated in more detail.
Results from electrochemical measurements performed between 650 and 800 °C showed that the performance was excellent of anode-supported SOFCs with a screen-printed porous CGO interlayer and a PSCF cathode. Even at 650 °C, the area specific resistance was lower than 0.5 Ω.cm². The microstructure of the cathode and the performance of this type of SOFC were not obviously affected by variations in the sintering temperature of the cathode. Higher electrochemical performance, in particular in the temperature range 650 – 750 °C, was achieved by applying a thin and dense CGO interlayer using reactive sputtering (RS) – or electron beam physical vapor deposition (EB-PVD).

3.4 Key topic: fuel processing systems

3.4.1 Objectives and fields of activity

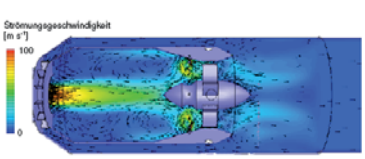
The availability of hydrogen is a prerequisite for the use of fuel cells in mobile and stationary applications. At present, however, an infrastructure for hydrogen as a future energy carrier does not yet exist. It is therefore essential that hydrogen is produced from readily available energy carriers. For stationary applications, natural gas and heating oil are suitable sources, while for mobile applications, gasoline, kerosene and diesel are options. Currently, the energy carriers listed above are mainly produced from the fossil primary energy carrier crude oil. In the long term, biomass will be used to produce part of the liquid energy carriers needed today.

In IEF-3, research in the field of fuel processing concentrates on reforming middle distillates such as kerosene, diesel, light heating oil, and diesel-like biofuels. For use in the generation of electricity or on-board power in portable or mobile applications (APU: auxiliary power unit), the fuel that is used to drive the vehicle must also be used to drive the fuel cell APU system. For aircraft applications, kerosene and jet fuel for light aircraft are the only fuels available, and yet they are allowed to contain a high level of sulfur-containing components. In the field of fuel processing, theoretical and experimental studies are therefore conducted on the desulfurization of liquid fuels and their vaporization.

For on-board power supply in the 5- $kW_{el.}$ power class, activities concentrate on the autothermal reforming of kerosene, diesel and fuels similar to diesel. Process engineering analysis, component development and system design are important components of the R&D activities. Reformers are being developed for high-temperature SOFCs and low-temperature PEFCs at 80 °C as well as for high-temperature PEFCs (160 °C – 200 °C).

The fuel that is produced by reforming has a high carbon monoxide content of up to 10 vol.%. In a reactor connected downstream from the reformer, steam is used to convert the carbon monoxide into additional hydrogen and carbon dioxide. The product gas with a carbon monoxide content of 1 vol.% can be fed directly into an HT-PEFC after cooling to 180 °C.

All areas of work are supported by relevant modeling activities. Important tools are CFD simulations on the Jülich supercomputers and system simulations using the Simulink program in order to optimize the dynamic performance under load changes and for starting strategies.



3.4.2 Important results

3.4.2.1 Desulfurization

At IEF-3, work began on the desulfurization of liquid fuels in 2005. The focus is on the desulfurization of kerosene and light heating oil (EL) with a maximum of between 3,000 ppm and 2,000 ppm sulfur-containing hydrocarbons. Following a theoretical analysis and the selection of processes that are generally suitable for local desulfurization in fuel cell systems, the individual processes were then examined on a laboratory scale. Using results from experiments, two processes were found to be particularly effective. Hydrodesulfurization with presaturated hydrogen in the liquid phase is the only process that has the potential to be technically implemented in the short term. In the medium to long term, a combination of membranes and adsorbents could also play an important role in desulfurization. However, more research is required on this area.

Fig. 85 shows how the single molecules react with hydrogen. One hydrogen molecule reacts with the sulfur atom in the thiophene ring and forms hydrogen sulfide. A second hydrogen molecule saturates the previous sulfur bond with the two carbon atoms in the thiophene ring. The graphic illustrates this for 2,5,7-trimethyl-benzothiophene and a simple thiophene. The products formed are butadiene and a multiply alkylated benzene molecule. The chemical reaction equations for this are as follows:

$$C_4H_4S + 2\,H_2 \rightarrow C_4H_6 + H_2S$$

$$C_{11}H_{12}S + 2\,H_2 \rightarrow C_{11}H_{14} + H_2S$$

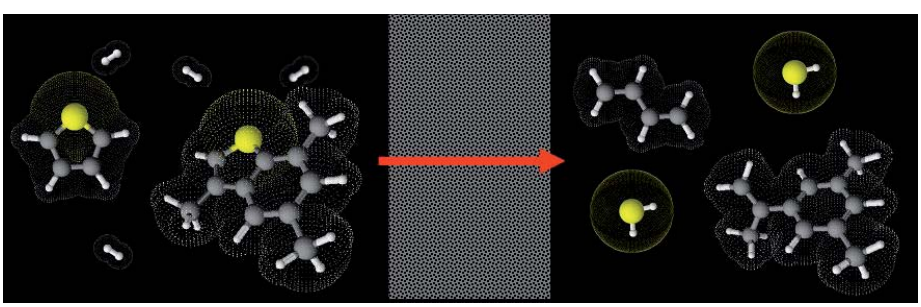


Fig. 85: Schematic of hydrodesulfurization with hydrogen using a catalyst (gray-black dotted areas)

These reactions occur in the gas phase or in the liquid with presaturated hydrogen. In the liquid phase, absolute pressures of 40 – 75 bar and temperatures of 330 – 390 °C are required. For the desulfurization of the kerosene commercially available in Europe with approx. 550 ppmw S, hydrogen partial pressures of 25.5 bar are necessary.

An eye must also be kept on the further development of adsorbents and membranes for the desulfurization of liquid fuels. Suitable materials must be tested in order to ascertain whether desulfurization is possible at lower temperatures and pressures than required for hydrodesulfurization with presaturation.

After specification, kerosene is permitted to contain up to 3,000 ppmw sulfur. As an intermediate in the refinery, kerosene with a concentration of approx. 1,675 ppm S is obtainable. This is a maximum value. The main components of that fuel were identified as approx. 600 ppmw dimethyl- and trimethyl-benzothiophene and 450 ppmw monomethylated and dimethylated benzothiophene, respectively. In commercially available Jet A-1, which is a refinery product made from kerosene and additives, significantly reduced concentrations of thiophenes (150 ppmw) and mono- and dimethylated benzothiophenes (100 ppmw each) are found. Trimethyl-benzothiophenes are one of the main components in Jet A-1 (approx. 200 ppmw S), while only 100 ppmw were found in the kerosene sample with 1,675 ppmw S.

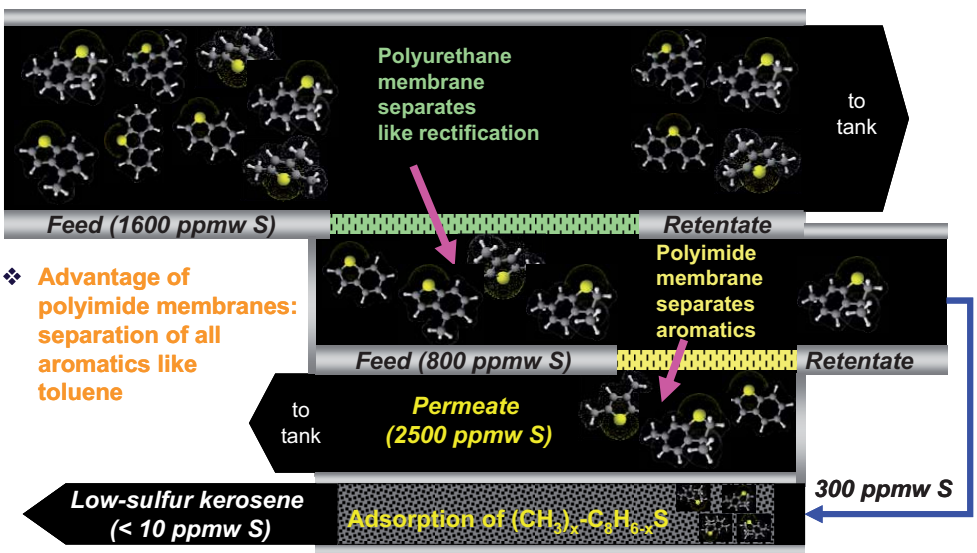


Fig. 86: Schematic of a multistage process for desulfurization using membranes and an adsorbent for deep desulfurization (gray-black dotted areas)

Fig. 86 shows how such types of kerosene can be desulfurized with membranes. The first step involves using a polyurethane-polyacrylonitrile composite membrane to retain the multiply alkylated benzothiophenes and the dibenzothiophene from the product on the low-pressure side. In the next step, a polyimide membrane is used to perform a pervaporation with a desulfurized permeate. This initially reduces the level of sulfur from 1,600 ppmw down to 600 – 700 ppmw, and subsequently to 200 – 350 ppmw. The remaining sulfur – composed of mono-methylated benzothiophenes and thiophenes – must then be separated by adsorption. A detailed description of these experiments and the results obtained are provided in Chapter 4.3.

3.4.2.2 Component development

A reformer for middle distillates was developed in IEF-3 over the past few years and is shown in Fig. 87. This reformer is capable of using standard diesel fuels to produce a sufficient quantity of hydrogen for fuel cells with a power between 3 und 5 kW_{el}. The

preferred process for this is known as autothermal reforming. The reformer has a cold-starting device, internal steam generation, and a device for extracting the process heat that arises during reforming.

In order to gain a better understanding of the flow and temperature conditions inside the mixing chamber of the reformer, and to be able to predict them more easily, **c**omputational **f**luid **d**ynamics (CFD) modeling is carried out at Jülich. CFD modeling aims to generate precise data on the temperatures reached in the mixing chamber and on the local zones in which the fuel is vaporized under the given reaction conditions, such as temperature, flow rates of air, steam and diesel fuel, and the spray pattern of the nozzle. The CFD-based approach used to design the reactor was also adapted for catalytic combustion.

Fig. 87: Diesel reformer

Fig. 88: Catalytic burner before final assembly

In fuel cell systems, different exhaust gases are produced in different operating states. All of the gases have one factor in common: they contain residual combustible gases, which cannot be released into the environment. Their low-emission combustion is performed in a catalytic burner. The reaction heat produced is used to generate steam for the system. In steady-state operation, for example, only 80 – 85 % of the hydrogen generated in the fuel processing system can be converted in the fuel cell. The residual hydrogen and the combustible components carbon monoxide and methane must be almost fully converted in the burner with a conversion level of more than 99.5 %. In such cases, the fuel cell exhaust gas contains approx. 9 vol.% H_2, 1.5 vol.% CO and 0.3 vol.% CH_4. In normal operation, the catalytic burner generates approx. 10 m³/h exhaust gas with a residual oxygen concentration of approx. 1.4 %. The methane conversion characteristics are used to design the catalytic burner. The design assumes a liquid hourly space velocity of 20,000 $m^3_N/m^3_{Kat}/h$. The incorporation of turbulence structures ensures a thorough mixing of the gas flow and improved heat transfer, as the interfaces that form as a result of laminar flow are broken up. The turbulence structures are attached to the external tube surfaces. Between the enveloping bodies, an annular gap is formed through which the steam-water mixture can flow. Fig. 88 shows the most important components of the burner before catalyst installation and final assembly.

The main challenge connected with the design of the burner is maintaining the upper operating temperature on the burner side at 450 – 750 °C and the complete evaporation of water on the evaporator side. The device must be designed in such a way that it can meet these requirements. Suitable models were calculated on the Jülich supercomputer.

Fig. 89 - Fig. 94 provide an overview of the temperature profile, the flow pattern, the spray pattern (distribution of droplets), and the evaporation intensity in the evaporator in the catalytic burner assuming the reflection of the droplets at the heat exchanger surface (CFD model: reflect wall function). In this system, only around one twentieth of the injected water is evaporated, whereby one eighth of the heat flow required for full evaporation and superheating is transferred. The heat flow across the impact surface therefore only amounts to one twentieth of the target value. This is due to a variety of different factors. The water droplets that hit the impact surface are reflected back into the spray chamber, causing a mist to form, as shown in Fig. 91. Only slight heat transfer occurs during reflection, so that the droplets do not evaporate on the impact surface. In the mist, the droplets have a homogeneous residence time distribution. The injection of water leads to the formation of a large vortex-like flow in the spray chamber. In the area around the channel junction, a small vortex is created rotating in the opposite direction. These two vortex structures ensure that the majority of droplets remain in the spray chamber and do not enter the channel. The droplets flow with the large vortex, although some of the droplets in the junction area end up in the vortex rotating in the opposite direction. From here, they are then either carried back or they enter in the channel. The majority of droplets remain in the spray chamber. The uniform flow ensures a homogeneous mixing of the steam in the spray chamber. The water vapor has a fairly homogeneous temperature of around 150 °C.

The droplets are heated by the steam, whereby the heat flow over the impact surface into the spray chamber only proves sufficient to evaporate individual droplets. The heat transfer coefficient at the impact surface is very small, as the heat transfer occurs directly from the wall to the superheated steam. Above all, the droplets that evaporated are those that flowed over the heating surface in the vortex beforehand, which leads to the curved profile of the evaporation intensity in the spray chamber as shown in Fig. 92. Over time, more and more droplets collect in the spray chamber. At the base of the nozzle, a dead volume emerges with a temperature of less than 100 °C. Here, water vapor condenses out, which amplifies the problem of the accumulating water. An evaporator with a deflector plate should improve the performance of the burner (Fig. 93 und Fig. 94).

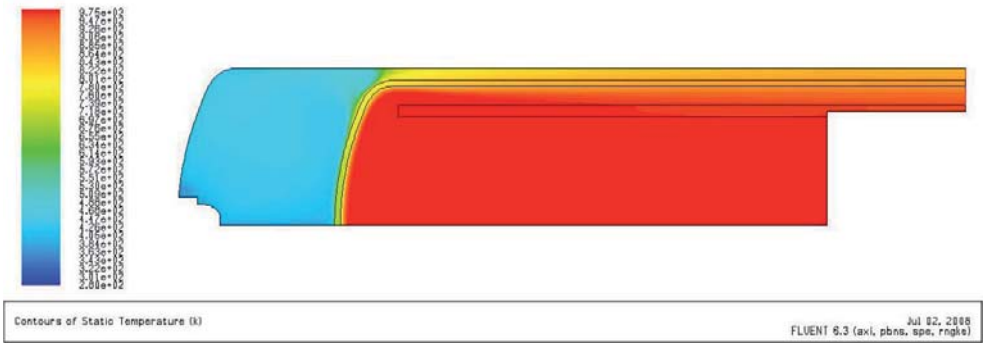


Fig. 89: Temperature profile for the reflect wall function, [K]

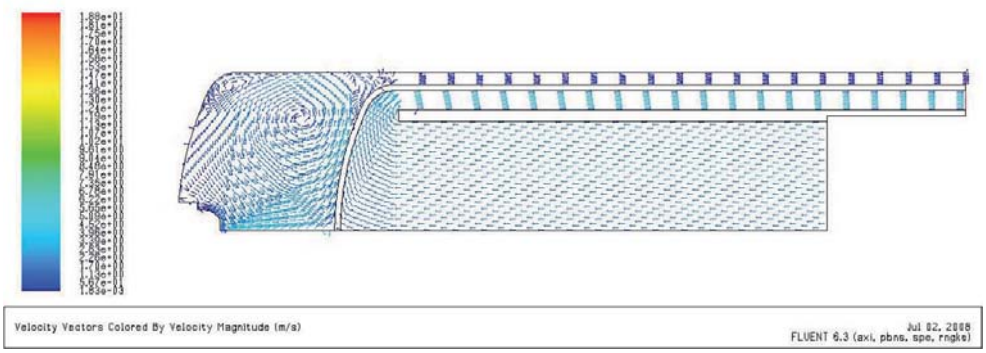


Fig. 90: Velocity vectors for the reflect wall function, [m/s]

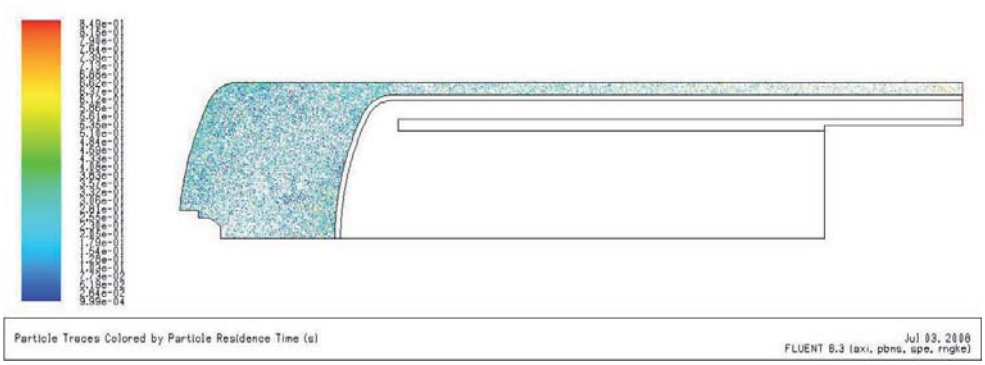


Fig. 91: Droplet traces for the reflect wall function, residence time [s]

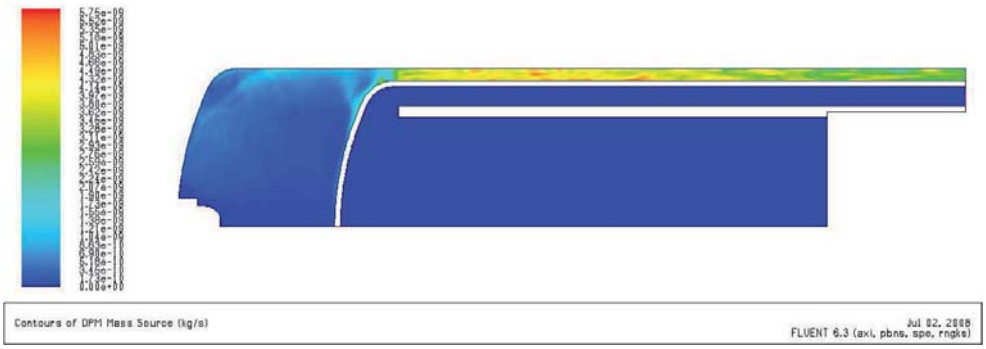


Fig. 92: Evaporation profile for the reflect wall function, [kg/s]

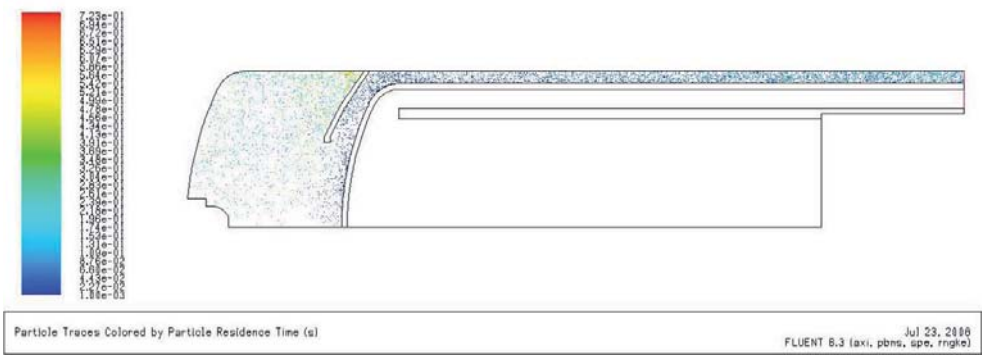


Fig. 93: Droplet traces with deflector plate for the wall-jet wall function, residence time [s]

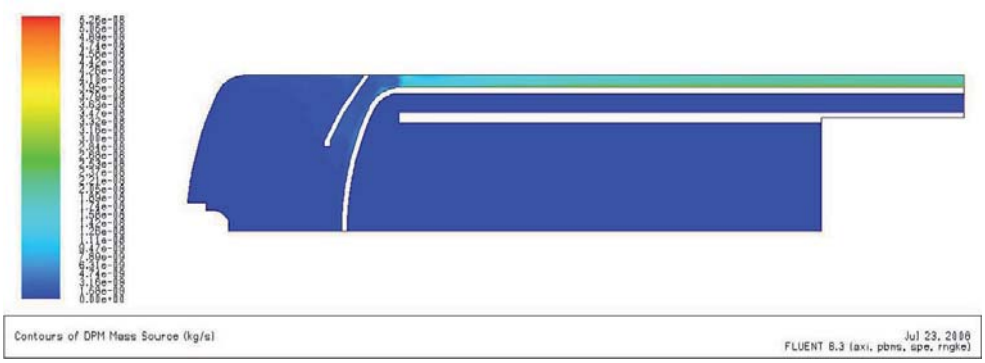


Fig. 94: Evaporation profile with deflector plate for the wall-jet wall function, [kg/s]

3.4.2.3 System development

One important tool for system development is the modeling of all basic components in fuel cell systems with reforming. This modeling covers SOFCs, PEFCs and HT-PEFCs. The emphasis is on modeling all subcomponents, primarily components with integrated heat exchange and phase transformation, as well as on static and dynamic system simulations. The aspects examined are the start-up process and behavior during load change. Within the scope of process analyses, water balances were calculated as a function of external conditions such as relative humidity and ambient temperature. The HT-PEFC system with autothermal reforming of Jet A-1 provides an electric power of 5 kW. The operational data for the HT-PEFC are as follows:

- current: 625 mV;
- temperature: 180 °C;
- anode conversion level for H_2: 84 %
- cathode air ratio: λ=2

An efficiency of 80 % was assumed for both the compressor and the pumps. Differences in the quantities of water were determined on the basis of the temperature difference between the condensation temperature of the mass flow and the environment. The difference between the two sides of the condenser in this case was assumed to be no more than 20 K. The pressure is the respective system pressure. The result in this case is the difference between the amount of water that could be condensed in this manner and the water requirements of the system. Negative values represent a deficit. The water balance of the system is shown in Fig. 93 as a function of relative humidity for four different ambient temperatures. The operating pressure of the system in this case is 1 bar.

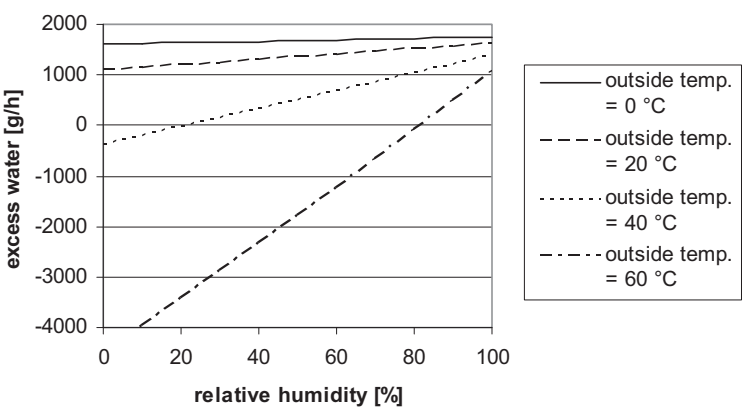


Fig. 95: Water balance of the HT-PEFC system with ATR of Jet A-1, p=1 bar

Fig. 95 shows that if we assume a temperature difference of 20 K in the condenser, the water balance for the ambient temperatures 40 °C and 60 °C results in a deficit. The increasing humidity reduces the deficit but the system's water requirements are not covered at an ambient temperature of 60 °C and a humidity of less than 80 %.

Further analyses have shown that it is possible to achieve a positive water balance by operating at higher pressures, even for higher ambient temperatures. If we take a location with an ambient temperature of 50 °C at a temperature difference of 20 K, or 15 K at 55 °C, then a system pressure of 2 bar is required at a relative humidity of 65 % in order to close the water balance. Calculations with a pressure of 3 bar show that even for an ambient temperature of 40 °C, the water balance for all relative humidity values was positive. At an ambient temperature of 60 °C, the water requirements can be covered at a relative humidity of 40 % and above (Fig. 96).

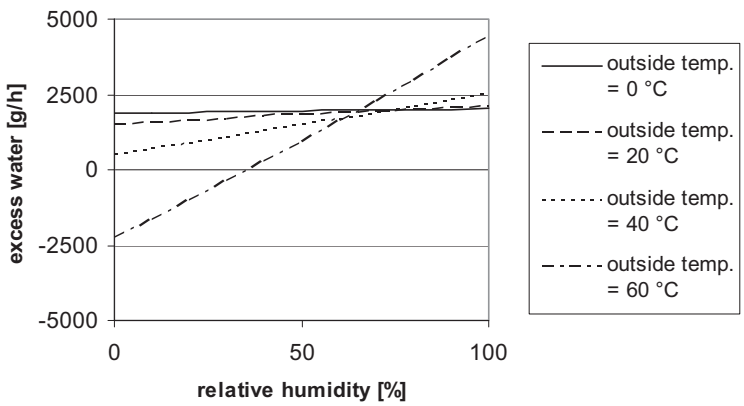


Fig. 96: Water balance of the HT-PEFC system with ATR of Jet A-1, p=3 bar

A detailed evaluation of global weather data for the average monthly values in the period from 1961 to 1990 and the thirty-year maximum show that the water balance can be closed in many locations at temperatures of less than 40 °C and a humidity greater than 20 % without pressurizing the system. These climate conditions roughly correspond to the average conditions in Riyadh, Saudi Arabia, in September or those in Las Vegas during the hottest month of July.

3.4.3 Staff members and fields of activity

Name	Tel. (+49 2461-61-) E-mail-address	Field of activity
Prof. Dr. R. Peters	4260 ra.peters@fz-juelich.de	Head of Fuel Processing Systems
C. Döll	6481 c.doell@fz-juelich.de	Reforming of kerosene, GTL and BTL fuels
R. Menzer	6708 r.menzer@fz-juelich.de	Process engineering systems calculations and analyses

Dr. J. Pasel	5140 j.pasel@fz-juelich.de	Head of the Industrial Chemistry for Fuel Processing Group
Dr. R. C. Samsun	4616 r.c.samsun@fz-juelich.de	Head of the Systems Engineering for Fuel Processing Group
F. Scharf	5322 f.scharf@fz-juelich.de	CFD modeling, diesel reforming
A. Tschauder	4547 a.tschauder@fz-juelich.de	Reactor development, reforming, system design
Y. Wang	2779 yo.wang@fz-juelich.de	Desulfurization of kerosene and heating oil

3.4.4 Important publications, PhD theses and patents

Important publications

Peters, R.

Fuel Processors

in Handbook of Heterogeneous Catalysis, Eds. Ertl, G.; Knözinger, H.; Schüth, F.; Weitkamp, J., Wiley-VCH, Weinheim, (2008)

The handbook (8 volumes) is a collection of review articles which provide an overview of the current state of the art of the multifaceted and interdisciplinary field of heterogeneous catalysis. The “Fuel Processors” Chapter describes the existing level of scientific knowledge from the feedstock to system applications for fuel processing. The topics addressed are the thermodynamics of reforming, desulfurization, different reforming techniques, CO fine cleaning, and system development. In the area of methanol steam reforming, the processes in the active centers of the catalyst are described, as is the development of a 60-kW_{th} compact reformer (with a lower heating value of H_2).

Peters, R; Latz, J.; Pasel, J.; and Stolten, D.

Desulfurization of Jet A-1 and Heating Oil: General Aspects and Experimental Results

ECS Transactions, 12 (1) 543-554 (2008)

This paper describes a range of potential processes for the desulfurization of kerosene and light heating oil in the liquid phase. These include hydrofining with presaturated hydrogen, adsorption, fractionated distillation, and membrane and extraction processes. Using the first laboratory experiments in this area, the application potential of these processes in fuel cell systems is discussed.

Porš, Z.; Pasel, J.; Tschauder, A.; R. Dahl, R.; Peters, R. and Stolten, D.

Optimised Mixture Formation for Diesel Fuel Processing

Fuel Cells, 08 (2) 129-137 (2008)

This paper provides a detailed description and discussion of the development of a mixing chamber for diesel, water vapor and air. On the basis of the state of the art of diesel reforming, which is characterized by a diesel conversion of 99 % after 200 h and heavy deposits around the nozzle of the reformer, a description is provided of the flow simulation of the mixing chamber and visual verification. Long-term experiments followed the completion of the development phase. With conversions of 99.7 % after 1,000 h, they underline the benefit of this method. By analyzing the operated apparatus and comparing the results with other CFD calculations, other design improvements can be implemented. Flow experiments in glass reactors with flow-like alternative media are used to derive the residence time behavior in the reactor chamber. This is required for dynamic simulations in software packages such as Matlab or Simulink.

Peters, R.; Grube, Th.; Pasel, J.; Samsun, R.C.:

Einsatzgebiete und technische Voraussetzungen für Brennstoffzellen in APU-Anwendungen
(Fields of use and technical prerequisites for fuel cells in APU applications)

Schriften des Forschungszentrums Jülich, Reihe Energie & Umwelt, Band 12, ISBN 978-3-89336-533-3, Der 4. Deutsche Wasserstoff Congress 2008, Tagungsband, Stolten, D.; Emonts, B.; Grube, Th. (Hrsg.)

Fuel cell APUs are one option for generating electricity efficiently with low emissions. In aircraft applications, for example, significant quantities of kerosene and thus CO_2 can be saved compared to conventional gas turbine technologies. In order to use fuel cell APUs, the framework conditions must be taken into consideration. These conditions consist of a combination of the application in question, the required electric power and the fuel to be used. Shipping has the largest power range to be covered from 5 kW_e to 5 MW_e. Most applications, however, have a power ranging from 5 to 50 kW_e. Fuel cell APUs have a good chance of developing into a marketable product if they are run on fuels for which infrastructures already exist, for example, gasoline, diesel or kerosene. The hydrogen required must then be produced from these fuels by means of a suitable reforming process. For the demonstration of a fuel cell_APU a wide range of combinations is possible for different fuel cell types with different reforming processes. From today's point of view, a fuel cell system based on autothermal reforming combined with an HT-PEFC will achieve extremely promising engine efficiencies of between 32 % and 36 % faster and much sooner than any other system combination.

Latz, J.; Peters, R.; Pasel, J.; Datsevich, L.; Jess, A.

Hydrodesulfurization of Jet Fuel by Pre-saturated One-Liquid-Flow Technology for Mobile Fuel Cell Applications

Chemical Engineering Science 64 (2008) 288 - 293

To prevent catalysts in fuel cell systems from poisoning by substances containing sulfur, the fuel used must be desulfurized to a maximum of 10 ppm sulfur. Diesel fuel for road vehicles within the EU is already desulfurized at the refinery. However, kerosene or jet fuel is permitted to contain up to 3,000 ppmw sulfur. Since the

hydrodesulfurization process used in refineries is not suitable for mobile applications, the aim of the present work is to develop an alternative desulfurization process for kerosene and to determine its technical feasibility.
To this end, many processes were assessed with respect to their application in fuel-cell-based auxiliary power units (APUs). Among them, hydrodesulfurization with presaturation was selected for detailed investigations. Laboratory tests revealed that syngas operation is also possible without any performance loss in comparison to operation with pure hydrogen. Pure hydrogen is not available in a fuel cell system based on the reforming of jet fuel. The effects of reaction temperature, operating pressure and liquid hourly space velocity (LHSV) were investigated. Different jet fuel qualities with up to 3000 ppm sulfur were desulfurized to a level of 15–22 ppm.
Finally, the technical applicability of hydrodesulfurization with presaturation was demonstrated in a pilot plant. In a 200-h experiment, a commercial jet fuel with 712 ppm sulfur was desulfurized to a maximum sulfur content of 10 ppm. The jet fuel contained the same amount of chemically bound hydrogen required in a fuel cell to achieve an electric power of 5 kW. The aim of developing a suitable process for the desulfurization of jet fuel in fuel cell APUs has therefore been achieved.

Wang, Y.; Latz, J.; Dahl, R.; Pasel, J.; Peters, R.

Liquid Phase Desulfurization of Jet Fuel by a Combined Pervaporation and Adsorption Process

Fuel Processing Technology, in press

Since the conventional hydrodesulfurization process employed in the refinery industry is not suitable for mobile fuel cell applications (e.g. auxiliary power units, APUs), the present study aims to develop an alternative process and determine its technical feasibility. A large number of processes were therefore assessed with respect to their application in fuel cell APUs. The results revealed that a two-step process combining pervaporation and subsequent adsorption is the most promising. Six different membrane materials and ten different adsorbents were screened in order to identify the most suitable and promising candidates. Further laboratory experiments were conducted to optimize the operating conditions and to collect data for a pilot plant design. Different jet fuel qualities with up to 1,675 ppm sulfur were desulfurized to a level of 15–22 ppm. The aim of developing a suitable process for the desulfurization of jet fuel in fuel cell APUs has therefore been achieved.

Pasel, J.; Meißner, J.; Porš, Z.; Samsun, R.C.; Tschauder, A.; Peters, R.

Autothermal reforming of commercial Jet A-1 on a 5 kW_e scale

International Journal of Hydrogen Energy 32 (2007) 4847 – 4858

Three reactors with different designs were used for the autothermal reforming of an alkane mixture and of commercial desulfurized Jet A-1. The reactors mainly differed from each other in terms of the design of the fuel vaporizer and educt mixing chamber. Suitable reaction parameters such as the molar $(H_2O)/(C)$ and $(O_2)/n(C)$ ratio were derived using a statistical experimental design. Load change experiments showed that the reformate flow altered with the external conditions without any measurable delay. This can be explained by the very fast kinetics of the partial oxidation of the hydrocarbons. Experiments on the long-term stability of the reforming reactions revealed that it is essential that the reformer possess a highly sophisticated evaporation and mixing chamber. This saw the achievement of very promising long-term stabilities for autothermal reforming of commercial desulfurized Jet A-1. The conversion of hydrocarbons over 500 h was 100 % without any detectable signs of deactivation. A slight decrease in activity was observed when operation continued. Nevertheless, 99 % Jet A-1 had been converted by the end of the experiment after 2,000 h.

Pasel, J.; Latz, J.; Porš, Z.; Meißner, J.; Samsun, R.C.; Tschauder, A.; Peters, R.

Autothermal Reforming of Jet A-1 and Diesel: General Aspects and Experimental Results

ECS Transactions 12 (1) (2008) 589 - 600

This paper deals with the general aspects and experimental results of autothermal reforming of Jet A-1 and diesel fuel. A process analysis based on the “pinch-point methodology” compares three different reforming routes, namely steam reforming, partial oxidation, and autothermal reforming. The analysis is based on a combination of these routes with a high-temperature polymer electrolyte fuel cell (HT-PEFC). Specifications of different fuels suitable for reforming applications are also given. Constraints regarding their suitability for autothermal reforming are also discussed. Accompanying experiments on the long-term stability of the reforming reactions revealed that it is essential that the reformer possess a highly sophisticated evaporation and mixing chamber. This saw the achievement of very promising long-term stabilities for autothermal reforming of commercial desulfurized Jet A-1. 99 % Jet A-1 had been converted by the end of the experiment after 2,000 h.

PhD theses

Latz, J.

Entschwefelung von Mitteldestillaten für die Anwendung in mobilen Brennstoff-zellensystemen
(Desulfurization of Jet Fuel and Marine Gas Oil for Application in Mobile Fuel Cell Systems)

Schriften des Forschungszentrums Jülich, Reihe Energie & Umwelt, Band 14,
ISBN 978-3-89336-535-7, RWTH Aachen University 2008

Fuel cells are well suited for generating on-board power supply in aircraft, ships and heavy goods vehicles to improve the energy efficiency and to cover rising demands for electrical energy. In order to operate fuel cells with the fuels available on board, the fuel is converted into a hydrogen-rich gas by a process of catalytic reforming. Since both the catalysts in the reformer and also in the fuel cell are deactivated by the sulfur compounds contained in the fuel, the fuel must be desulfurized. Whereas diesel fuel for road vehicles within the EU is already desulfurized at the refinery, jet fuel is permitted to have up to 3000 ppm of sulfur worldwide and marine gas oil for fueling vessels on inland waterways can contain up to 1000 ppm in the EU. Consequently, on-board desulfurization is required for the use of fuel cell auxiliary power units (APUs) on aircraft and ships. Since the hydrodesulfurization process used in refineries is not suitable for mobile applications, the present work had the aim of developing alternative processes and determining their technical feasibility. To this end, a large number of processes discussed in the literature were assessed with respect to their application in fuel cell APUs and four potentially suitable processes selected for detailed investigation. Laboratory tests revealed that adsorption in combination with separation by means of distillation or pervaporation is a suitable process for the desulfurization of jet fuel. Additionally, hydrodesulfurization with presaturation provided convincing results on a laboratory scale. In order to verify the technical applicability of fuel cell APUs, three desulfurization processes were assessed with respect to energy demand, size and durability. Of these processes, hydrodesulfurization with presaturation provided the best results. Whereas the technical application of the process consisting of adsorption and pervaporation requires further research work, the process of adsorption and separation by means of distillation is not economically feasible, above all due to the high energy demand.

Finally, the technical applicability of hydrodesulfurization with presaturation was demonstrated in a pilot plant for a fuel cell APU with a power of 5 kW_{el}, going beyond the laboratory scale. The aim of developing a suitable process for the desulfurization of jet fuel in fuel cell APUs has thus been achieved. However, the investigations on marine gas oil showed that desulfurization in fuel cell APUs is not possible at present even with the alternative desulfurization approaches currently available.

Samsun, R.C.

Kerosinreformierung für Luftfahrtanwendungen
(Reforming of Kerosene for Applications in Aviation)

Schriften des Forschungszentrums Jülich, Reihe Energie & Umwelt, Band 11, ISBN 978-3-89336-531-9, RWH Aachen University 2008

This thesis deals with fuel gas production from kerosene for fuel cells. Among other things, fuel cells can contribute significantly to the reduction of emissions from an aircraft in flight or on the ground. A special approach was developed to deal with the broad content of the topic in acceptable depth. The main focus was placed on the reforming process since the reformer can be considered as the heart of the system. However, the operation of the complete fuel processing system plays a key role in the success of the system. Therefore a comparable amount of attention was devoted to the fuel processing system. In order to carry out detailed analyses on the above-mentioned levels, namely the reformer level and the system level, two tools were selected: experiment and simulation. The reforming process was examined by means of extensive experiments, whereas studies on the complete system were supported by simulations. Firstly, the specifications of the fuel kerosene Jet A-1 were analyzed to obtain a better understanding of the physical and chemical characteristics of this substance. Using this knowledge as a basis, a reaction scheme was developed to describe the reforming process. Models for the necessary components of the various fuel processing systems were developed and verified experimentally. Using statistic simulations, the reactor components were optimized and subsequently combined to create fuel processing systems with a high level of heat integration. Realistic operating conditions such as system startup and the load change characteristics were simulated using dynamic simulations. In addition, the characteristics of the different reformers, the transient behavior and the long-term performance were also tested. The simulations show that the fuel processing system for a solid oxide fuel cell (SOFC) is much simpler compared to other systems. The system for a polymer electrolyte fuel cell (PEFC) is complicated due to the many components it contains. Operation under dynamic conditions is very difficult and requires an advanced control system. The system for a high-temperature polymer electrolyte fuel cell (HT-PEFC) has advantages over the PEFC system under dynamic operation conditions. The experiments with desulfurized kerosene Jet A-1 showed that an excellent quality product gas can be produced for 500 h with the ATR 7 reformer. With the ATR 8 reactor, a conversion level of 99 % was achieved after 2,000 hours of operation. Startup experiments showed that the startup time is mainly limited by the external steam preparation mechanism. Load change experiments showed that the ATR 5B reformer exhibits excellent behavior under tough load change conditions.

Important patents

Patent applications:

Principal inventor	PT	Description
Dr. Z. Pors	1.2272 PCT	Process for vaporizing a liquid fuel and a mixing chamber for performing this process
Dr. Z. Pors	1.2281 EP	Apparatus for producing a fuel oxidant mixture
Dr. J. Latz	1.2314 PCT	Process for purifying mineral oil fractions and an apparatus suitable for carrying out the process
Dr. J. Latz	1.2353	Process for purifying mineral oil fractions and an apparatus suitable for carrying out the process

Patents granted

Principal inventor	PT	Description
Dr. S. Montel	1.1965	Reactor with sieve-like bodies and method for operating said reactor
Dr. Z. Pors	1.2168	Reformer mixing chamber and method for operation thereof
Dr. Z. Pors	1.2169	Reformer mixing chamber and method for operation thereof

3.5 Interdisciplinary topic: process and systems analysis

3.5.1 Objectives and fields of activity

If highly efficient fuel cell systems are to be successfully developed for the market, then trends in energy supply in the energy use sector and the development of competitive technologies must be taken into consideration.

In terms of methodology, relevant well-founded assessments of energy carries are based on the description of stages in complete process chains with their respective characteristic conversion losses and environmental impacts. Activities in IEF-3 are devoted to a detailed process analysis of process steps that have not yet been adequately described. This concerns, for example, the provision of second-generation biogenic fuels with respect to their potential in terms of volume and also the conversion efficiency during production. With regard to the use of fuel cell systems in mobile, stationary and portable applications, another priority in terms of analysis work is the comparison of such systems with their respective competing technologies. Detailed cost analyses are also performed for this purpose.

New topics within process and systems analysis are those related to the production and use of biogenic fuels and a comparative assessment of vehicle drives. For auxiliary power units (APUs) with fuel cells in selected applications in the transport sector, the option of reforming biogenic fuels is to be investigated. Process and systems analysis supports this process by identifying suitable fuel paths, taking account of factors such as efficiency and the technological availability of the production process, as well as the biomass potential and fuel costs. The second key area involves analyzing in detail the prospects for mobile fuel cells compared to advanced internal combustion engines and hybrid drives, as well as electric drives based on sophisticated battery technologies, using dynamic simulations.

3.5.2 Important results

3.5.2.1 Mass-specific costs of systems with fuel cells

In almost all areas of application, fuel cell systems have to compete with established technologies. Costs that are higher than those of the competing technologies are therefore only feasible if the benefits are significantly greater. In order to control and manage product-oriented system development, cost forecasts that take a large number of factors into account are therefore extremely important. Corresponding forecasting methods should be easier to apply than an object-specific detailed cost analysis. However, they must also deliver results that are much more accurate than those of power-based cost estimates commonly used today or methods on a system level based on learning curves.

Within the scope of a PhD thesis, component-based relationships between masses and costs were analyzed in relation to other parameters and used as the basis for a modified mass-specific cost analysis in order to make well-founded estimates of the production costs. In contrast to conventional methods, it is not the entire system but rather individual components that are analyzed in terms of their cost-mass ratio, and cost-relevant component-specific secondary and tertiary criteria are also taken into account. The individual results are then combined in order to determine the cost of the system on the basis of different production rates. As the component costs are used as distribution functions in the

specially developed calculation model, the result of the calculation is also a distribution function.

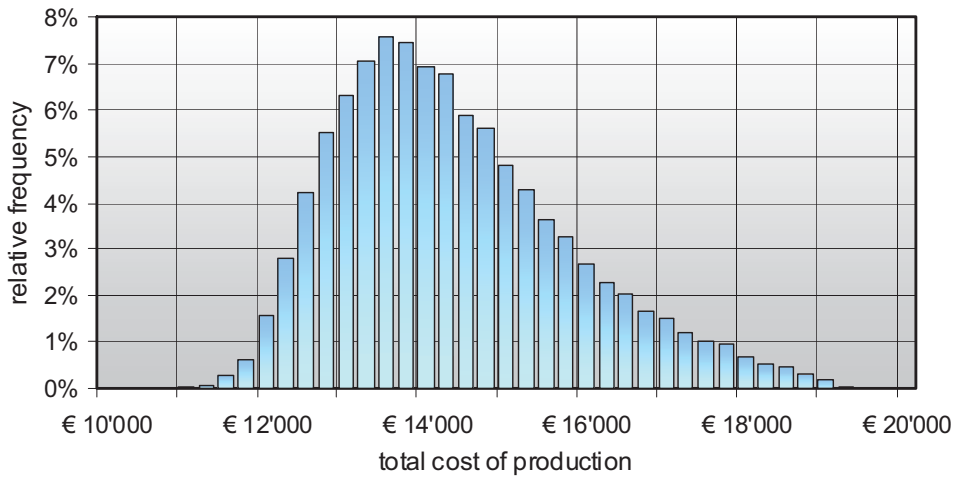


Fig. 97: Distribution function of the predicted production costs for a 1-kW$_e$ DMFC system for a production rate of 10,000 units per annum

Fig. 97 shows the result of applying the calculation model. To summarize, it was found that by using the methodology developed here, significantly better results were achieved compared to conventional mass-specific cost estimates. The limitations of this method can be found above all in components for which the cost-mass correlations could not be unambiguously determined, for example in the extremely low mass range.

3.5.2.2 Costs of energy services provides by fuel cell systems

In terms of the costs of energy services using systems with fuel cells in stationary and mobile applications, an existing calculation model was further developed and the database updated. The evaluation was based on the capital recovery factor as an instrument of dynamic investment appraisal. For vehicle drives with fuel cells, the price per kilometer is calculated, while for stationary systems generating electricity, the cost per kilowatt hour is calculated. Particularly in the area of stationary applications, a number of different applications must be taken into account according to the power range and characteristics of the power and heat requirements. Even legal regulations, such as the German law on combined heat and power (KWKG) and the law on the priority of renewable energies (EEG), play a role in the revenue structure and were integrated into the model.

In the area of vehicle applications, the calculations were used as a basis to determine projected additional costs for vehicles assuming the same costs per kilometer. Fig. 98, for example, shows that under the boundary conditions applicable here with a hydrogen price comparable to gasoline, the projected additional costs for hydrogen fuel cell vehicles depending on the price of gasoline lie on average between € 8,000 and € 15,000.

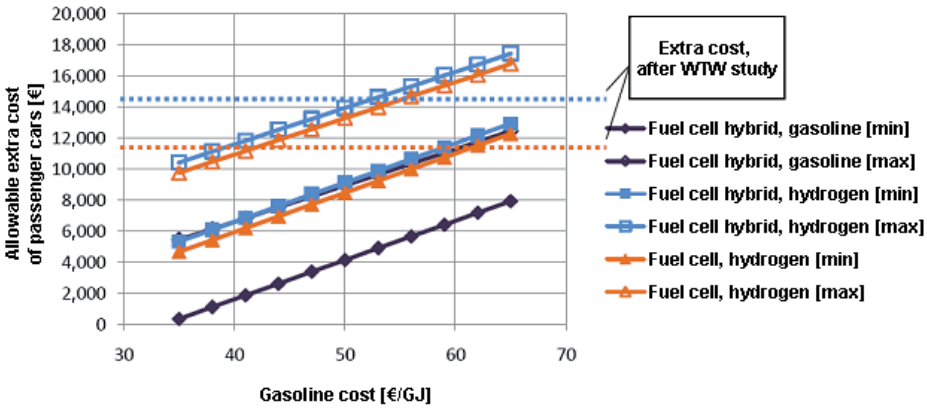


Fig. 98: Projected extra costs for vehicles with different drive configurations as a function of the price of gasoline with no additional costs for hydrogen

3.5.2.3 Prospects of making hydrogen available in NRW

Designing and constructing the future scenario in the energy sector, which will be oriented towards the use of hydrogen (H_2) as a storage and transport medium for energy with low climate-gas emissions, demands substantial changes in the infrastructure of the energy supply sector. A forecast of the expenditure required from the private sector and the national economy is complex and on the customer side depends first and foremost on the demand for H_2 as a function of time, which in turn is a function of the parameters of provision (costs, physical availability). In order to estimate this expenditure, assumptions must be made with regard to the applications of H_2 (H_2 sinks) that will appear over time and their development in terms of volume and market size.

On the supply side, depending on the demands of the user as well as regional and local circumstances, different supply pathways could prove to be more or less advantageous. Such options can be differentiated according to

- primary energy used,
- H_2 production technology,
- H_2 transport and distribution structure.

An important role could be played – particularly during the introduction phase of H_2 as an energy carrier – by H_2 as a by-product of industrial processes. Special conditions apply here regarding the appraisal in terms of money, which could promote the cost-effective provision of H_2. The same holds for existing infrastructural elements, which could emerge, for example, as a result of industrial exchanges.

Due to its unique starting position, the federal state of North Rhine-Westphalia (NRW) commissioned a study on the “Prospects of gradually setting up an H_2 infrastructure in North Rhine-Westphalia in a cost-optimized manner”, which is being conducted by the Wuppertal Institute for Climate, Environment and Energy and IEF-3.

[1,000 Nm^3/ d]	NRW total	Total [%]	NRW potential	Total [%]
Total volume	10,786	100	958	100
Chlorine electrolysis plants	1,732	16	810	85
Refineries	1,602	31	56	6
Other	5,691	53	92	10

Data for the whole of NRW and for the potential derived from this including deductions for the use of H_2 as a process gas

Tab. 3: H_2 volume in NRW

Tab. 3 shows the volumes of hydrogen determined from industrial sources in NRW. It can be clearly seen that chlorine electrolysis only accounts for 19 % of the total volume. The potential assessment, calculated after the deduction of H_2 volumes used among other things as process gas, gave rise to a figure of 85 % for chlorine electrolysis.

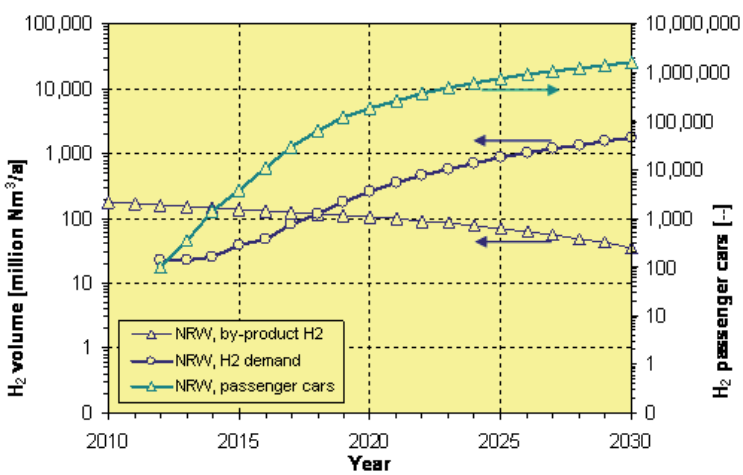


Fig. 99: H_2 balance for the volume of residual hydrogen and H_2 demand in NRW

The figures ascertained for NRW can be related to a time-dependent demand for H_2 in NRW, which can be determined on the basis of scenarios for the market introduction of H_2 vehicles and NRW-specific population trends and the development of vehicle density. Fig. 99 reveals that as far as the figures go, the demand for H_2 in NRW will exceed the supply from industrial sources from 2018 onwards for the present boundary conditions.

In the further course of this study, the need for investment in order to set up the appropriate H_2 infrastructure in NRW will be estimated and used as a basis to predict H_2 costs.

3.5.2.4 Comprehensive and dynamic evaluation of fuel cell technologies

Within the framework of the BMWi-funded project EduaR&D, the subproject headed by VBZ (R. Menzer) and VSA (T. Grube) entitled “Comprehensive and dynamic evaluation of new energy technologies and their potential using fuel cell technology as an example” led to the following overall technology evaluation of stationary natural-gas-based fuel cells:

None of the available natural-gas-based stationary fuel cell systems would be able to survive on the market at the moment (PAFC, PEFC, MCFC, tubular/planar SOFC). The relatively complex situation regarding a technological and economic evaluation demands a fundamental and comparative analysis of the current state of the art, the potential, options and their feasibility in order to be able to better predict forthcoming technological challenges.

In order to quantify the remaining time to successful market introduction and penetration to estimate the chances of success and to derive funding recommendations, the following process analysis steps were considered necessary:

- identification of key system deficiencies
- process engineering analysis of standard fuel cell systems
- identification of systems technology optimization options
- identification of options for expanding the application spectrum, and
- identification of the main criteria for a quantitative technology evaluation.

The PEFC and tubular SOFC are fraught with inherent system deficiencies. This is the reason why it will take longer from the outset to develop these systems into competitive systems than it will the HT-PEFC, MCFC and planar SOFC. The PEFC requires external reforming heated by natural gas, whereby part of the natural gas used is then no longer available for the intrinsic electrochemical process. This factor gives rise to a loss of power of approx. 30 % and is the real reason for the low system efficiency of approx. 35 %. The tubular SOFC exhibits a high ohmic resistance as a result of the electron flow in the circumferential direction of the tubes. This leads to a high voltage drop of approx. 100 mV, which can only be compensated by a low current density.

Throughout the two-year project, our understanding of fuel cell systems based on the PEFC, MCFC, tubular/planar SOFC was increased using energetic system simulations. The commercial software CYCLE-TEMPO (inc. fuel cell computational module) and PRO/II (in-house fuel cell computation module) were used for this purpose. The analyses covered the following areas:

- Standard CHP: generation of power and heat extraction (full load, parameter variation, optimization, partial load performance)
- Options: process heat (MCFC and SOFC), turbine integration (for gas turbine in pressure mode) and in situ CO_2 separation (SOFC)
- Compared to the natural gas situation today, the option of operating the system with hydrogen gives rise to huge advantages for the PEFC and actually represents a knockout criterion for the MCFC (CO_2 demand not covered).

The main criteria for evaluating the technologies were identified and subjected to a detailed comparative analysis:

- specific system weights in kg/kW (stack, BOP, other), and
- net system efficiencies, as they directly affect the system weight (resulting from 8 steps consisting of power and voltage losses, internal energy consumption and losses).

In the literature, the targets for specific investment costs for fuel cell systems range for example from € 1,000 – 1,250 (1,500) per kW. If we consider that

- the competing technologies are also being further developed, and
- that a clear advantage must exist in order to displace competing technologies,
- then we are looking at a target of around € 1,000 per kW (hypothesis 1).

Present-day mass production of cars shows that weight-specific investment costs cannot be reduced at will. For Europe, the average is € 12 per kg. This value is three times higher for gas motors. This figure of approx. € 40 per kg is also considered a useful estimate for fuel cell systems for the future mass production of fuel cells. Anything below this value is regarded as unrealistic unless certain technological circumstances emerge (that cannot be foreseen today) which would give rise to such a situation (hypothesis 2).

Here, the fact that both low-cost and expensive materials are used in fuel cell systems must be taken into account. If we take the planar SOFC as an example, the interconnect material would cost approx. € 5 – 10 per kg (in the future) and the cathode material around € 100 per kg. Another argument for hypothesis 2 involves the characteristics of the PAFC. Although the PAFC was not analyzed in detail in the EduaR&D project because it is believed to have little prospect of success, it should be noted that the large number of PAFC systems produced (nearing mass production) has already led to the envisaged low weight-specific investment costs of approx. € 40 per kilo becoming a reality.

These considerations gave rise to a target of 25 kg/kW for the specific system weight.

The current state of the art today for the stack and the BOP has led to three classes of specific weights, all of which are still above the target weight of 25 kg/kW:

- approx. 200 kg/kW: tubular SOFC
- approx. 100 kg/kW: PEFC, MCFC, and the first pilot plants based on the planar SOFC
- approx. 100 kg/kW: HT-PEFC/assumed starting point, as no system is currently available (simple system, power density similar to PAFC)
- approx. 50 kg/kW: for planar SOFC in a second pilot plant achievable immediately by means of selected material savings (without further development)

The reduction rates for weight still required are thus as follows (rounded up):

- factor of 2 to 3 (planar SOFC)
- factor of 4 (PEFC, MCFC), and
- factor of 8 (tubular SOFC),

Based on the previous analysis, the planar SOFC has particularly good chances of achieving these targets. Negative experience with fuel cell systems that have been around for some time led to the following recommendations for further development:

- focusing of further development on a laboratory and pilot plant scale until the target weight of 25 kg/ kW has been achieved (duration: approx. 10 years), and
- abandonment of early large-scale demo projects.

There is still a long way to go before today's technologies become competitive. Series production alone (without stack and system development) and the hope of "learning as we go along" are not enough to achieve the target costs in an acceptable period of time or with acceptable capital investment.

Finally, for a basic comparative system assessment – taking account of the past as well – we created uniformly structured fuel cell development diagrams (road maps) with generally valid time axes. This revealed a remarkable phenomenon, namely that in all cases the technological ideas/problems/solutions tended to occur during the same phases:

- improvement in the respective electrochemical process itself
- progression towards a technological cul-de-sac
- new orientation/development leap
- further development and gradual pursuit of future options, and finally
- hidden in the future: success or failure of the respective fuel cell system.

3.5.3 Staff members and fields of activity

Name	Tel. (+49 2461-61-) E-mail address	Field of activity
Th. Grube	5398 th.grube@fz-juelich.de	Drive simulation, process and systems analysis
Dr. J. Werhahn (until 2008)		Mass-specific cost analysis, systems analysis

3.5.4 Important publiications

Important publications

Werhahn, J.; Grube, Th.; Stolten, D.

Mass-Specific Cost Calculations for Fuel Cell Systems: A New Way to Predict System Costs

Poster, Fuel Cell Seminar 2007, San Antonio, USA: 15.10.2007 – 19.10.2007

Reducing costs is still one of the biggest challenges facing fuel cell technology in terms of developing new market-oriented applications. Detailed information on the cost structures and cost drivers of such systems is therefore becoming increasingly important. Against this background, there is a considerable need for cost models which function without having to design a concrete system – including the production sequence – but which simultaneously achieve an accuracy that far exceeds simple characteristics-based processes on a high level of aggregation. A method developed

in this context for modified mass-specific cost forecasts determines the cost distribution of the components and the complete system, and also incorporates the dependency on production rates. The analyses are based on the empirical values of the mass-specific costs of system components and their transformation in concrete distribution functions, which allows a detailed error analysis to be performed as well as a better statistical localization of the results. The poster presents the methods and relates them to other methods of forecasting the costs of fuel cell systems.

Grube, Th.; Pastowski, A.

Strategien des kostenoptimierten Aufbaus einer Wasserstoff-Infrastruktur in Nordrhein-Westfalen

2nd Aachener Congress, Decentralized Infrastructure, Water – Energy – Waste, 28 – 29 October 2008 The vision of exploiting hydrogen for the climate-friendly generation of energy in the future cannot be separated from producing this hydrogen on the basis of renewable energies. However, it may make sense to draw on hydrogen that is produced in a different way in industrial processes for a transition period. This applies particularly when there is insufficient use for the hydrogen produced in this manner. As hydrogen is already produced and used for a variety of different purposes, it lends itself well to use in future stationary and mobile energy applications. In producing, distributing and using hydrogen, existing infrastructures can be used, creating synergies, and thus allowing the cost-effective creation of an early infrastructure for energy. In NRW, the Rhein-Ruhr district is not just an urban area that is in an excellent position to pioneer the use of hydrogen for energy purposes. More importantly, industries are concentrated in this region which generate and use hydrogen and already have an existing infrastructure. The study presented here was conducted on behalf of the federal state of NRW. It relates the amount of H_2 available from industry as determined in a survey with a model of the construction of an H_2 infrastructure in NRW and emphasizes NRW's unique starting position.

Grube, Th.; Höhlein B.; Menzer, R.

Assessment of the Application of Fuel Cell APUs and Starter-Generators to Reduce Automobile Fuel Consumption

FUEL CELLS 07 (2007) Electric power for various types of drives can be provided for different mobile applications with low emission levels and high degrees of efficiency using auxiliary power units (APUs) based on fuel cells. Demand for this is increasing in line with the growing need to provide electricity for luxury and safety features, as well as steering and control functions. Furthermore, APUs are promising in terms of a low level of emissions for higher levels of efficiency when installed in trucks for on-board power supply. The advantages and disadvantages of fuel cell APUs are shown in comparison to conventional electricity generating technologies in terms of their deployment in cars on the basis of dynamic drive simulations.No. 2, p.128-134

3.6 Interdisciplinary topic: analysis

3.6.1 Objectives and fields of activity

The Physicochemical Fuel Cell Laboratory develops and applies analytical techniques for the in situ and/or spatially resolved analysis of structures and effects. The basic structure-activity relationships of complex processes in fuel cells and reactors are determined and used to improve both. Furthermore, the physical properties of cell components are determined, which serve to verify and determine the mechanical and thermodynamic requirements for their use in fuel cells. The methods used in the fuel cell laboratory focus on the following areas:

- imaging analysis techniques
- spatially resolved analysis techniques
- physical analysis techniques

3.6.2 Important results

3.6.2.1 Imaging analysis techniques

During the period under review, different devices for imaging analysis were tested, selected and purchased in terms of their efficiency for the development of low-temperature fuel cells (DMFC and HT-PEFC) with help from experts in the field of microanalysis at IEF-2. The most important instrument was a field-emission scanning electron microscope (FE-SEM) coupled with energy dispersive X-ray spectroscopy (EDX). During the performance evaluation of the devices, some interesting results were obtained. For example, in element distribution images generated using EDX of an MEA that had been in dynamic operation for more than 50 hours in a scooter (Fig. 100), ruthenium was also discovered on the cathode side.

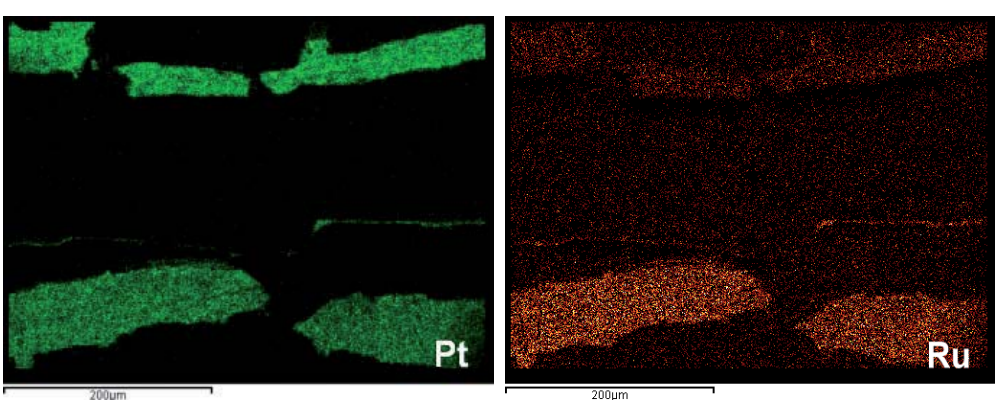


Fig. 100: EDX element distribution image for platinum (left) and ruthenium (right) in a DMFC MEA operated and aged in a scooter

Quantification of the ruthenium content on the cathode side, once again using EDX, revealed values of 0.88 mass % and 0.14 atomic %. These values are near to the detection limit of

EDX and should therefore be verified by a different analysis technique (e.g. in cooperation with ZCH). However, they also clearly support a migration of the ruthenium from the anode to the cathode side.

Fig. 101 shows the corresponding SEM micrograph of the cross section in backscattered electron mode. The cross section was created using a conventional grinding and polishing process involving prior cold embedding in epoxy resin. Cracks were detected in this cross section at the interfaces between membrane and catalyst layer. This immediately led to the question as to what extent these cracks could be caused by artifacts in the preparation, whether they were produced during the manufacturing process, or generated during operation. Due to a possible swelling of the Nafion membrane during the grinding and polishing process and subsequent shrinkage during the drying phase, these cracks could also have been introduced during preparation. It is indisputable that the interfacial adhesion in those areas where the cracks occurred must have been weakened beforehand in order for the cracks to appear at all during preparation.

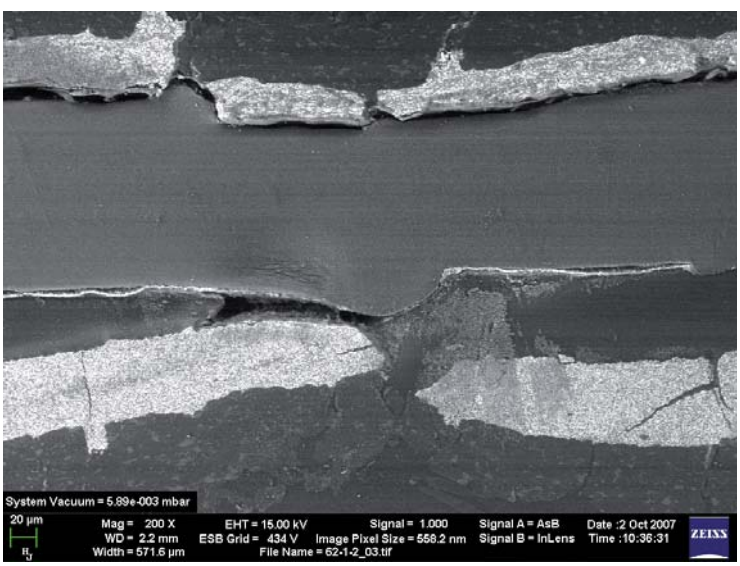


Fig. 101: SEM micrograph of a cross section of a DMFC MEA operated and aged in a scooter in backscattered electron mode

Fig. 102 shows a SEM micrograph of a cross section of a DMFC catalyst layer produced using ion-beam preparation. This innovative preparation technique enables mirror-like cross sections of heterogeneous coating systems of any roughness and porosity to be prepared as well as materials with varying hardness. The sample does not have to be embedded beforehand in epoxy resin, which means that the porosity of the catalyst layer emerges to a much greater extent than is the case for conventional cross sections. Moreover, it becomes clear that the low-energy argon ion beam causes almost no damage to the material.

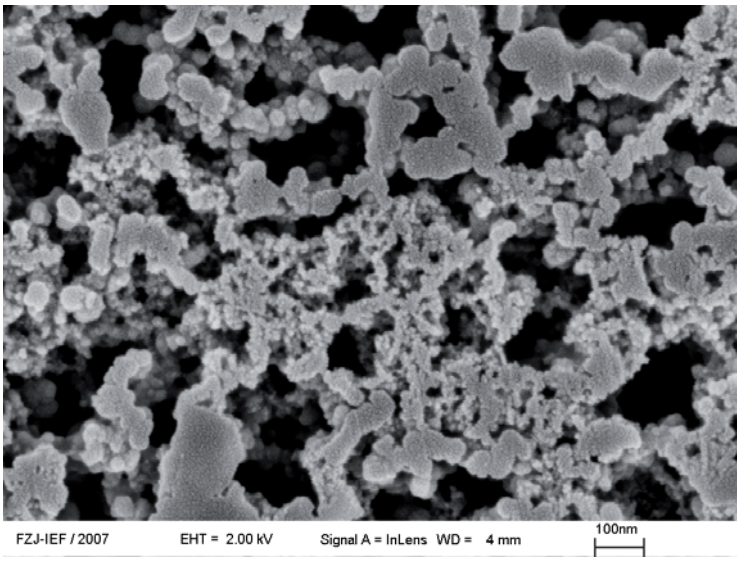


Fig. 102: SEM micrograph of a cross section of a DMFC carbon-supported catalyst layer produced using ion beam preparation

Furthermore, these images document the excellent high resolving power of the SEM used, which is manufactured by Zeiss. This is made even clearer in Fig. 103 by means of a top view of the carbon-supported catalyst layer. Catalyst particles or agglomerations of these catalyst particles measuring only a few nanometers can be clearly seen both in secondary electron mode, which reproduces the morphology of the layer, as well as in backscattered electron mode, which images the material contrast.

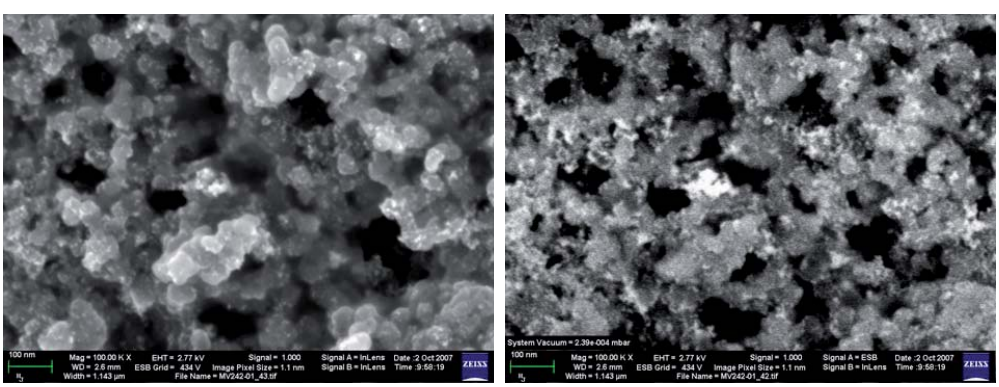


Fig. 103: SEM micrograph of a DMFC carbon-supported catalyst layer; top view of the morphology in secondary electron mode (left); top view of the material contrast in backscattered electron mode (right)

The acquisition of the SEM-EDX unit and the aforementioned preparation equipment provide a basis for imaging structural changes in low-temperature fuel cell components, for example changes caused by degradation, with a very high spatial resolution. This will help to increase the performance of fuel cells in the future.

3.6.2.2 Spatially resolved analysis techniques

Current distribution measurements with segmented cells

In close cooperation with ISEA (RWTH Aachen University), the measuring device for current distribution, temperature and impedance across the active cell area in direct methanol fuel cells was further developed. The media flows can now be automatically controlled and the geometry of the flow field plates has been modified to better suit the flow geometry of the stack cells. Fig. 104 shows two newly developed test cells with the respective circuit board for current segmentation. Both test cells are designed for a geometric electrode area of approximately 18 cm². The test cell (left) has flow field plates with double meander geometry, which is the same for both electrodes (Fig. 104, top left). The two meander channels allow a separate asymmetric media supply. Current is conducted through a printed circuit board with 28 gold-plated segment contacts (Fig. 104a, bottom). The test cell (right) has a meander structure on the anode side and a channel structure on the cathode side, as is also used in DMFC stack cells (Fig. 104, top right). Current is conducted through a printed circuit board with 25 segments (Fig. 104, bottom right).

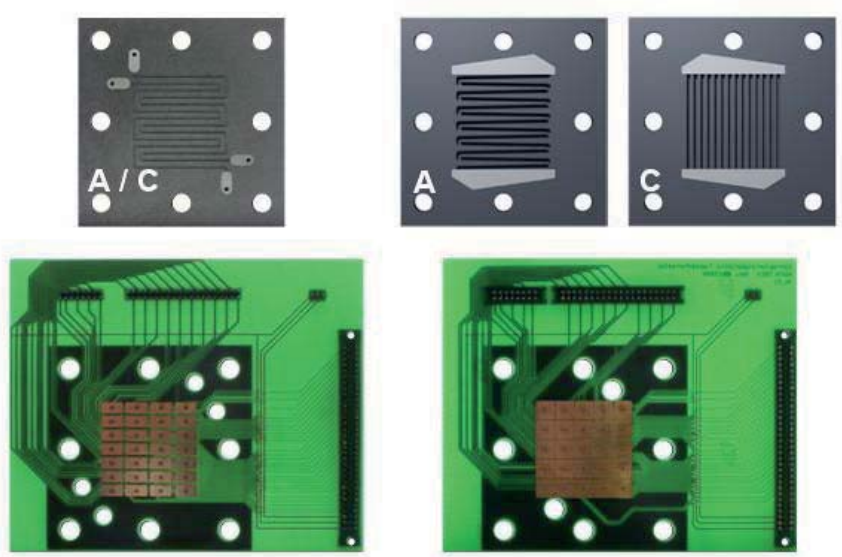


Fig. 104: Flow field plates (top) and adaptor circuit boards (bottom) for current distribution measurements with newly developed test cells

An advantage of the double meander geometry compared to the grid geometry used in the past is the more uniform distribution of current over the electrode area. Fig. 105 (left) shows the current distribution with a double meander cell under typical operating conditions. The ratio of the highest and lowest segment current is 1:4. The benchmark for the grid geometry in comparison is ≥ 1.7. Only when the media flows are reduced is the current inhomogeneously distributed. If we halve the air flow, for example, the result is oxygen depletion at the air outlet and a reduction in the local current (Fig. 105, right).

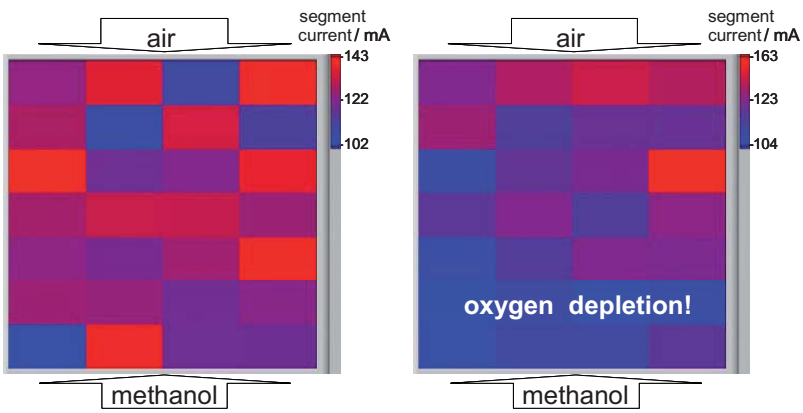


Fig. 105: Current distribution with a double meander cell; T = 70 °C, j = 200 mA/cm²; $\lambda_{MeOH} = \lambda_{air} = 4$ (left), $\lambda_{MeOH} = 4$, $\lambda_{air} = 2$ (right)

Magnetic tomography

A central issue associated with the technique of magnetic tomography is the uniqueness of the determination of the underlying current density using the measured magnetic field. In general this is not the case as there are current distributions that do not generate an external magnetic field (e.g. toroidal coil). For a fuel cell, the uniqueness was shown for a situation where a perpendicular flow of current through the MEA was assumed. This was then expanded to the fuel cell stack (Fig. 106).

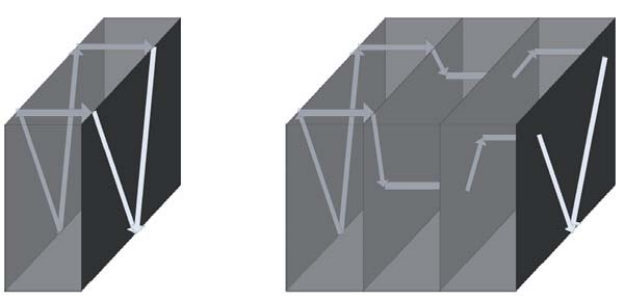


Fig. 106: Assumed current flow in a single cell (left) and in the stack (right)

The uniqueness proof was expanded into a structural algorithm in which those parts of the magnetic field were identified that were produced by currents in the end plates and the MEA. By exploiting jump relations, it is possible to estimate the current distribution in the MEA by taking limiting values when approaching the end plates.

3.6.2.3 Physical analysis techniques

The techniques described in this section can roughly be divided into two different areas:

- degradation
- material characterization

In terms of the area of “degradation”, the main instruments used are a climate chamber manufactured by Weiss Umwelttechnik and an environmental simulation chamber manufactured by Binder. The first instrument (Fig. 107) is currently being delivered and set up. The second was successfully tested for the necessary specifications. Without thermal loading, the maximum temperatures of -40 °C and +180 °C were achieved without overshooting the specified heating and cooling times of 180 and 90 minutes, respectively.

Fig. 107: WK3-600/40 climate chamber manufactured by Weiss Umwelttechnik GmbH

For the area of material characterization, the first results are now available for photon cross correlation spectroscopy. These results showed that Nafion® ionomer solutions with high ionomer concentrations exhibit a lower tendency to form agglomerations and a much better long-term stability (Fig. 108). This is relevant for DMFC fabrication, as improved long-term stability allow us to work with larger volumes and therefore lowers the costs associated with fabrication.

Other instruments and setups, including a material testing machine for determining mechanical properties, and equipment for thermal analysis and mercury-free standard porosimetry, are currently being constructed or tested. The first results are expected in the near future.

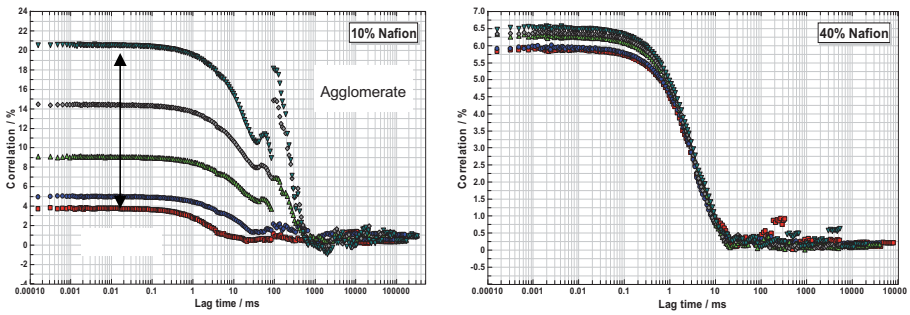


Fig. 108: Improved Nafion® ionomer solution properties for increased ionomer concentrations regarding agglomeration and stability determined by photon cross correlation spectroscopy

3.6.3 Staff members and fields of activity

Name	Tel. (+49 2461-61-) E-mail address	Field of facility
Prof. Dr. D. Stolten	3085 d.stolten@fz-juelich.de	Head of Fuel Cell Laboratory (i.PU)
Dr. H. Echsler	8710 h.echsler@fz-juelich.de	Imaging analysis techniques
K. Klafki	4832 k.klafki@fz-juelich.de	Conventional sample preparation
A. Schröder	1579 a.schroeder@fz-juelich.de	Studies on media and current distribution in the DMFC using electrochemical neutron-radiographic and X-ray-based methods
W. Sträter	3077 w.straeter@fz-juelich.de	Standard porosimetry
Dr. J. Wackerl	6228 j.wackerl@fz-juelich.de	Physical analysis techniques
M. Wannert	5590 m.wannert@fz-juelich.de	Development of mathematical procedures for magnetic tomography, reconstruction of current density distributions using 2D and 3D models and single cells
Dr. K. Wippermann	2572 k.wippermann@fz-juelich.de	Explanation of physical and chemical degradation mechanisms, spatially resolved measurements

3.6.4 Important publications

Important publications

Kulikovsky, A.A.; Schmitz, H.; Wippermann, K.

Direct methanol hydrogen fuel cell

Electrochemical and Solid-State Letters 10, 8 (2007) B126-B129

> We report on a regime of DMFC operation. At low air flow rates, the cell splits into three domains. Close to the inlet of the oxygen channel, the cell generates current in a “normal” DMFC mode (galvanic domain). Close to the outlet of the oxygen channel, the cell consumes current to produce hydrogen on the anode side (electrolytic domain). If the rate of hydrogen production is high, H_2 permeates towards the galvanic domain and contributes to proton production there. In other words, between GD and ED a domain operating as a hydrogen cell arises. In our experiments, direct methanol-hydrogen fuel cells exhibited performance comparable to DMFCs at half the air flow rate. The contribution of hydrogen oxidation to cell performance was supported by the analysis of the cell polarization curves. The “high-” and “low-voltage” curves are separated by a gap of the order of 100–200 mV. No other mechanism could explain such a dramatic difference. The peak in local current at the interface between the galvanic and electrolytic domains is another argument in favor of the mechanism of hydrogen oxidation.

Kulikovsky, A.A.

Direct methanol-hydrogen fuel cell: The mechanism of functioning

Electrochem. Comm., 10 (2008) 1415 - 1418

> At low air flow rates, the active area of a direct methanol fuel cell splits up into galvanic and electrolytic domains: the former generates current, while the latter consumes it to convert methanol to hydrogen. Recent experiments (A.A. Kulikovsky, H. Schmitz, K. Wippermann. Electrochem. Solid-State Lett. 10 (2007) B126) suggest that hydrogen can permeate towards the galvanic domain and contribute to current production there. Here, we perform an analysis of potential distribution in a cell. The analysis shows that between galvanic and electrolytic domains the transition region forms, which can operate as a hydrogen cell. This confirms the conjecture made in the cited paper.

Kulikovsky, A.A; Schmitz, H.; Wippermann, K.; Mergel, J.; Fricke, B.*; Sanders, T.*; Sauer, D.U.*

Bifunctional activation of a direct methanol fuel cell

J. Power Sources 173 (2007) 420–423

> Measurements of local current distribution in a cell with straight channels and segmented electrodes reveal the following effect. The decrease in the air flow rate below a critical value causes part of the DMFC to switch to electrolysis mode. Restoring the normal (super-critical) air flow rate returns the electrolytic domain to galvanic mode with increased galvanic performance. This bifunctional activation can be explained by the cleaning of the Pt surface on the cathode side by oxides and an increase in the number of electrochemically active sites on the anode side. Periodical lowering of the air flow rate below the critical value thus recovers cell performance.

This method of performance recovery does not require an external power source; at the time of activation, the galvanic domain plays the role of the power supply.

Sauer, D.U.*; Sanders, T.*; Fricke, B.*; Baumhöfer, T.*, Wippermann, K.; Kulikovsky, A.A.; Schmitz, H.; Mergel, J.

Measurement of the current distribution in a direct methanol fuel cell - Confirmation of parallel galvanic and electrolytic operation within one cell

J. Power Sources 176 (2008) 477–483

A measurement system has been developed which allows precise measurement of the current distribution in linear and square fuel cells. The unique feature of this measuring technique is that it is non-reactive with regard to current distribution. This was achieved by counterbalancing the voltage drop along the measurement shunt with a constant voltage source and an operational amplifier. Using the new measuring technique and a specially designed single-channel direct methanol fuel cell, the bifunctional regime of DMFC operation was directly observed for the first time. In this regime, part of the cell works as a normal fuel cell and the remaining part operates as an electrolyzer. The onset of this regime depends on the air flow rate. At low flow rates, the electrolysis process is very severe. Besides the single channel, a conventional square cell was segmented into 25 elements and the current distribution was measured here as well. Critical areas in the cell with reduced current production were identified easily. The new measurement system allows precise measurements to be taken of current distributions in hydrogen and direct methanol fuel cells. Based on this technique, important results have already been obtained in the first measurements. This technology could provide significant support for further developments and improvements of fuel cells.

Hauer, K.-H.*; Potthast, R.*; Wannert, M.

Algorithms for magnetic tomography—on the role of a priori knowledge and constraints

Inverse Problems, 24 (2008)

Magnetic tomography is concerned with reconstructing currents inside the fuel cell from their external magnetic field. This paper investigates a number of projection methods in combination with the Tikhonov regularization for stabilizing the solution of the Biot Savart integral equation Wj = H. In particular, we study the influence of a priori knowledge when incorporated into the choice of projection spaces, for example, divergence freedom or the integration of the boundary value problem. These reconstruction schemes are compared and the ill-posedness of each algorithm is analyzed in terms of the behavior of the singular values of the corresponding operators both when a priori knowledge is incorporated and when the geometrical setting is modified. Finally, we numerically evaluate the stability constants for fuel cell applications.

3.7 Interdisciplinary topic: quality management

3.7.1 Objectives and fields of activity

Quality-assurance measures are regarded as an integral part of work flows and are applied more and more frequently to ensure a high degree of development, production and characterization quality.

The most important objective behind the introduction of a quality assurance system (QAS) in the area of single cell measurements on the SOFC is achieving a high level of consistency, reproducibility and reliability of the measurement results. Reliable results and data are indispensible – not only for our own research and development, but also for that of our industrial partners (where important economic decisions must be made).

By introducing QAS, we can save time and money and guarantee the high throughput of single cell measurements. In addition, test conditions can be defined in such a way that comparisons between different samples are possible. In practice, unanimity has yet to be achieved on the test system and experimental conditions between external laboratories. This makes it difficult to compare the results from different laboratories at the moment. Therefore, the introduction of QAS is not just extremely important in our laboratories but also and, perhaps more importantly, we must convince external partners of the necessity of QAS in the area of single cell measurements.

3.7.2 Important results

3.7.2.1 Creation of a quality management system for fuel cell fabrication

On the basis of work performed at IEF-3 for a master's thesis on the topic of "Process-oriented quality management in fuel cell fabrication", a detailed plan was drawn up on the topic of quality assurance in manufacturing. The first step involved modeling the fabrication processes currently employed for membrane electrode assemblies (MEAs), stack components and stacks for the DMFC. For improved transparency, the production structure was subdivided into three core areas:

- incoming goods
- MEA fabrication
- stack production

Incoming goods includes materials received both for MEA fabrication as well as for stack production.

The production flows in the core areas of MEA fabrication and stack production can be broken down into seven groups:

- coating (10)
- membrane pretreatment (20)
- frame production (30)
- assembly (40)
- graphite processing (50)

- stack assembly (60)
- stack dismantling (70)

In order to make the process structure more readily comprehensible to the reader, the present fabrication processes are shown in a graphic. Fig. 109 shows the coating process as an example.

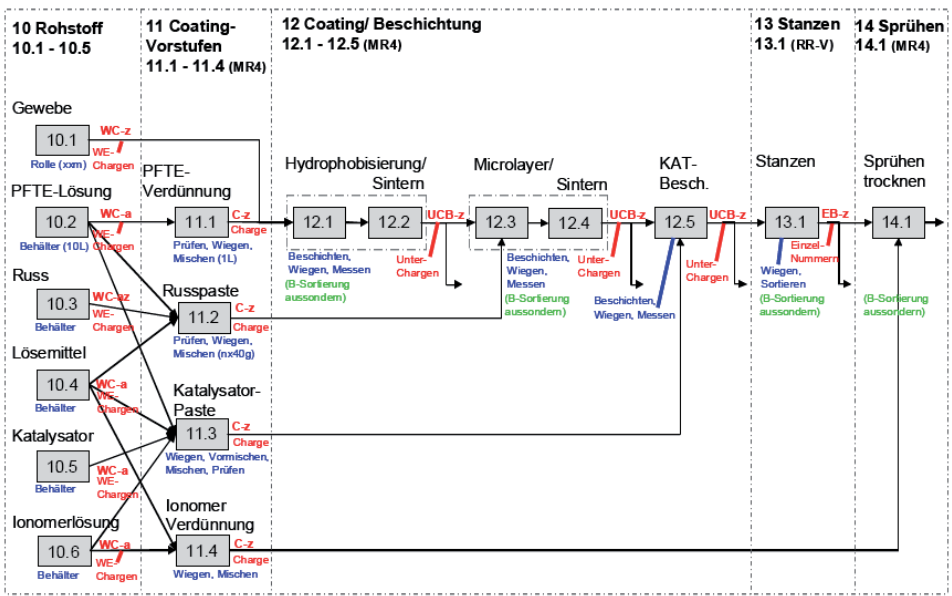


Fig. 109: The coating process (10) in MEA fabrication

After this study on the present status of fabrication, a concept was drawn up for a future data infrastructure in the fabrication process. The existing local data storage and data management were identified as significant weak points for reproducible and thoroughly transparent DMFC fabrication.

“Paperless documentation” with a central database will have to be created in order to ensure centralized and constantly updated data acquisition. Fig. 110 shows a possible data infrastructure.

Apart from computer-assisted data input at the individual stages of the coating process, it is also possible to read in data directly from the machines or to store data on RFID chips attached to the semi-finished products.

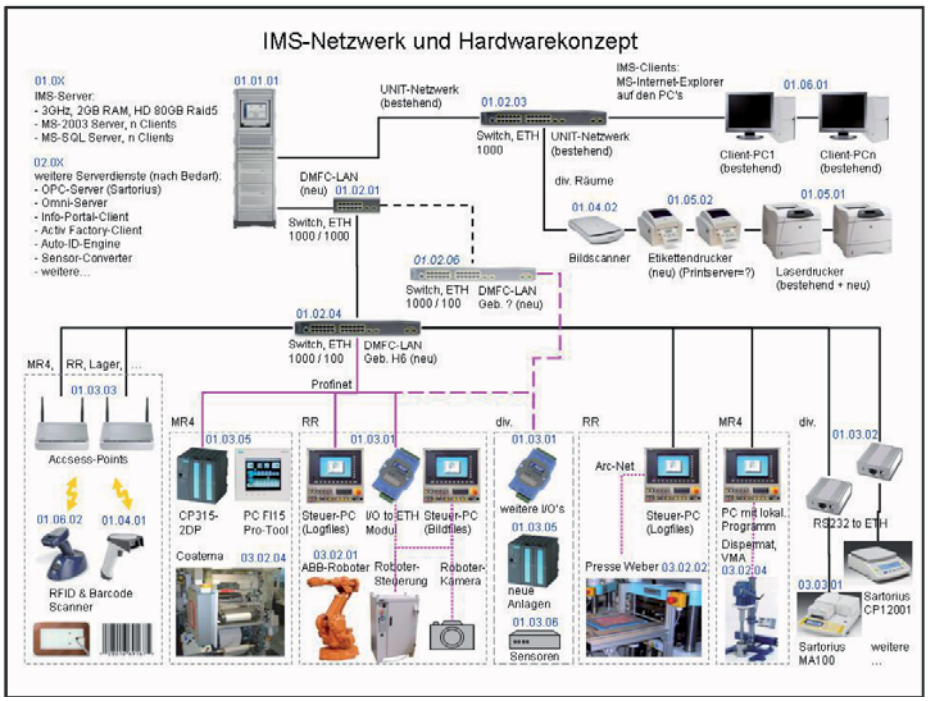


Fig. 110: Paperless documentation in DMFC fabrication

The implementation of such a system is broken down into several phases (Fig. 111). Fuel cell fabrication has already been fully structured. The database and data management are based on this structure. The time horizon for implementing such a project is in the order of two years.

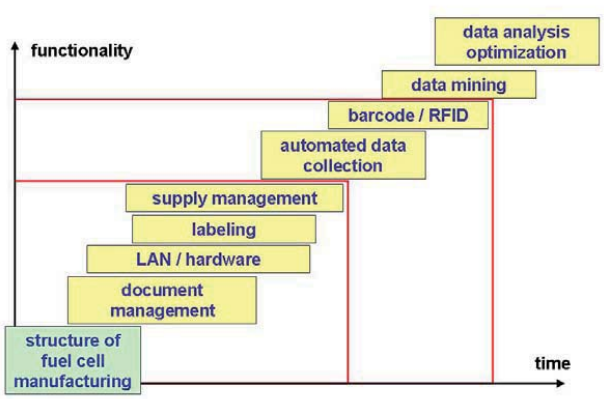


Fig. 111: Successive implementation of auto-ID technology

3.7.2.2 SOFC single cell measurements

A number of years ago, Forschungszentrum Jülich began setting up a quality assurance system in the area of single cell measurements. The first steps involved verifying the measuring system and optimizing the test and measurement conditions. Only then can the results of the single cell measurements be of a predefined quality level. This also means that the entire single cell measurement process will ultimately be standardized and prescribed. The necessary documentation for this already exists, for example procedure instructions, working instructions and inspection instructions, all of which are based on the DIN EN ISO 9000 standard. However, these specifications alone are not enough to guarantee a prescribed quality level. This is only possible if the cells are inspected as incoming goods – in other words, every fuel cell delivered must be examined and the framework conditions for cells must be predefined in a “cell specifications” document.

The most important “product” in the area of single cell measurements can be considered to be the measurement results, which are presented in reports. Such reports are characterized by a high level of uniformity and contain all of the relevant information required to correctly interpret the results. Only then will a quick comparison between measurement data be possible.

3.7.3 Mitarbeiter und Tätigkeitfelder

Name	Tel. (+49 2461-61-) E-mail address	Field of activity
Dr. M. Müller	1859 mar.mueller@fz-juelich.de	General quality management, quality assurance in the DMFC area
Dr. Vincent Haanappel	4656 v.haanappel@fz-juelich.de	General quality management, quality assurance in the SOFC area

4

Projects

Selected R&D Projects

- RuNPEM – On course for a DMFC with homogeneous media distribution
- Contributions for increasing reliability – The SOFC in long-therm test
- The use of mineral oil products in fuel cells – The desulfurization of middle distillates
- Zero-CO_2 use of fossil energy carriers – Optimized process for integrating CO_2 separation into the power plant process

4.1 RuNPEM – On course for a DMFC with homogeneous media distribution

4.1.1 Motivation

Under real operating conditions for a DMFC stack, inhomogeneous water and gas distribution across the cell area causes uneven current distribution. This effect does not just reduce stack power but it also impacts on the long-term stability of the single cells and the stack. We must understand media and current distribution in order to modify the operating conditions and the stack components in order to achieve as homogeneous a media distribution as possible and thus a higher power and lower degradation rates. The clear correlation between media distribution and current distribution under realistic conditions can only be achieved if both distributions are simultaneously measured *in operando*.

4.1.2 Methodology

An approach for spatially resolved current, impedance and temperature distribution was developed by the Institute for Power Electronics and Electrical Drives (ISEA) at RWTH Aachen University within the scope of a cooperation (see also 3.6.2.2). It is possible to simultaneously determine media and current distribution using the technique of *in operando* neutron radiography. This involves neutrons radiating through the direct methanol fuel cell during the current distribution measurement. The neutron beam that emerges behind the test cell is converted into light with a scintillation screen, projected onto the CCD sensor of a video camera, and read out using computer software. This technique involves the use of particularly strong incoherent scattering of the neutron beam on hydrogen atoms and weak scattering on test cell materials such as Al and C. In those areas where water droplets collect in the channels of the cathode flow field plates, this can lead to strong attenuation of the outgoing neutron beam and to a darkening of the color. In contrast, areas where the development of carbon dioxide at the anode dominates are much brighter. Other techniques for examining the formation of water droplets during DMFC operation are synchrotron tomography and radiography. These X-ray based methods are used to study selected areas in a fuel cell under operating conditions with a higher local resolution.

4.1.3 The “RuNPEM” project partners and research topics

The required X-ray-based and neutron-based *in operando* studies on direct methanol fuel cells were conducted in combination with spatially resolved current distribution measurements at Helmholtz Centre Berlin (HZB) as part of the BMBF-funded network “RuNPEM” (Röntgen- und Neutronenbasierte Untersuchungsmethoden für PEM-Brennstoffzellen; *X-ray-based and neutron-based test methods for PEM fuel cells*) for the period 2007 – 2010 (reference no.: 03SF0324D). Participating project partners and their main fields of work are shown in Fig. 112.

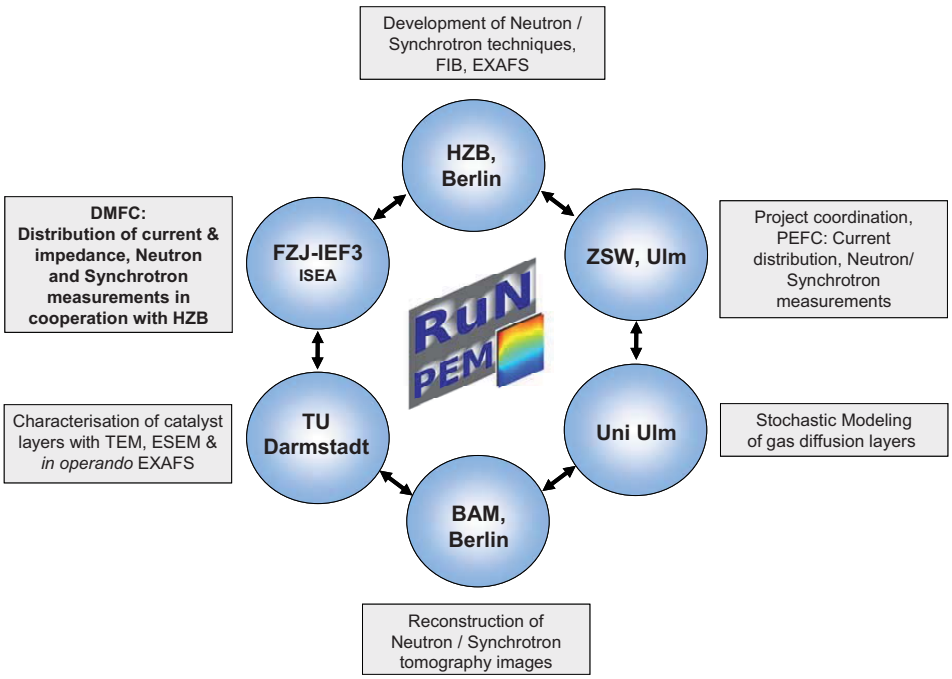


Fig. 112 Project partners and their main areas of research in the RuNPEM project

The focus of this work is on studying the influence of operating parameters (current density, temperature, flow rates, methanol concentrations) and the material characteristics and geometries of MEAs and flow field plates for local changes in the water management of the DMFC. The following material parameters are varied in the process:

- type of gas diffusion layer (GDL), i.e. carbon fiber, carbon fleece, carbon paper with and without a microlayer
- hydrophobic treatment of GDL (e.g. with PTFE)
- type of flow field plates (e.g. graphite, expanded graphite)
- design of the flow field plates (e.g. grid, meander or channel design, channel depth and width, channel-connector ratio, cell area)

The main objective is to identify favorable performance characteristics and material parameters for homogeneous distribution of media in the DMFC.

4.1.4 Neutron radiography combined with spatially resolved measuring techniques

In 2008, the first combined measurements of neutron radiography and current distribution were performed using DMFC single cells on the measuring device known as CONRAD (Cold Neutron Radiography and Tomography) at HZB in Berlin. The “cold” neutrons used in this system are characterized by increased interaction with matter and thus improved contrast in imaging.

Fig. 113 shows a photo of the equipment used in the CONRAD measurement chamber. The neutron beam sent out from the reactor falls on the left-hand side, passes through the screen, and hits the measurement cell, where depending on water and gas distribution it is weakened locally in the cell in different ways before it hits a detector and is converted to light. The light beam then hits the detector of a CCD camera. In the above-described manner, neutron radiograms are continually created with time intervals of a few seconds. These radiograms can then be correlated later with the current distribution images recorded simultaneously.

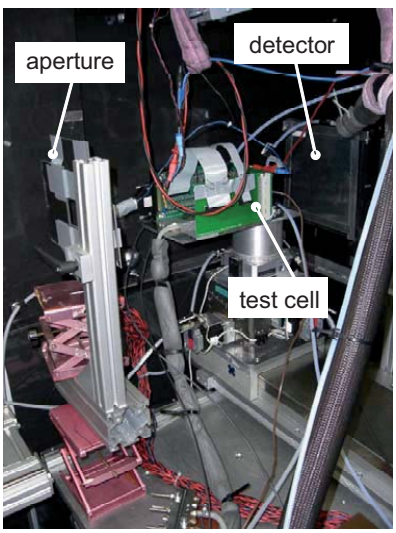


Fig. 113: Measurement setup for neutron radiography

The materials and thicknesses of test cell components are selected to minimize the scattering of the neutrons. The end plates of the test cells, for example, are fabricated from gold-plated aluminum instead of stainless steel because aluminum weakens the neutron beam four times less than iron. Hydrogen-containing layers in the test cells lying in the beam path must be kept as thin as possible. The thickness of the adapter board required for current distribution measurements therefore only measures 1 mm. Despite this, marginal scattering cannot be completely avoided, which is why normalized radiograms must be prepared. Here, the neutron radiogram of a test cell whose anode channels have been completely filled with methanol and whose cathode channels are free of water is used as a reference. The normalized radiogram can be generated by dividing the measured radiogram by the reference image.

Fig. 114 shows a comparison of the original image (left) and the corresponding normalized image (right) for a test cell with grid geometry when current is flowing. The channels in the anode and cathode flow field plates are either filled with water (methanol) or gas, for example, air on the cathode side and carbon dioxide on the anode side. As product water collects in the bottom and middle sections of the cell when current flows through the cathode channels, some of these cell areas appear dark in the images due to the reasons mentioned above. In contrast to this, the carbon dioxide that builds up in the anode channels in the top part of the cell make these areas appear brighter. In the normalized radiogram (Fig. 114,

right), the bright/dark contrast can be seen particularly clearly, and the interference effects of the test cell, such as the circular adhesive dots of the temperature sensors on the adapter boards (Fig. 114, left), disappear.

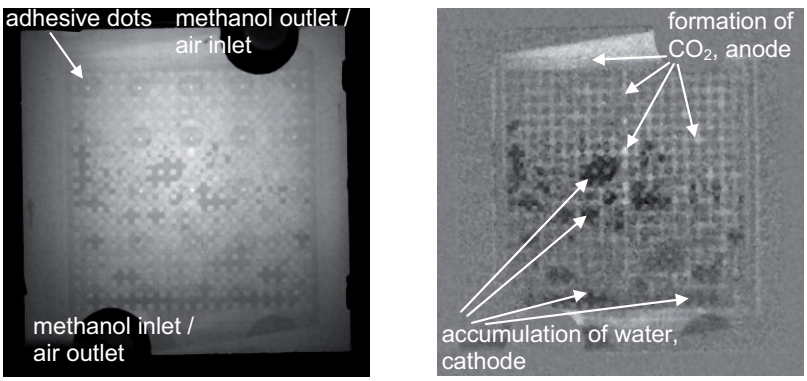


Fig. 114: Original neutron radiogram (left) and normalized neutron radiogram (right); temperature: 70 °C, current density: 300 mA cm^{-2}, $\lambda_{methanol} = \lambda_{air} = 4$, flow field plates: grid geometry

An example of the correlation between water distribution in the neutron radiograms and the current distribution measured simultaneously is shown in Fig. 115. Temporarily, such a large amount of water can be present in the cathode that a flooding effect occurs and the cathode channels in a large area of the cell are filled with water (see the neutron radiogram in Fig. 115, bottom left). This then inhibits the transport of oxygen in these areas and causes a corresponding slowing down of the oxygen reduction at the cathode catalyst. The result of this is that the segment current in the bottom and middle areas of the cell decreases strongly (Fig. 115, bottom right). As the total current remains constant, the segment current in the upper cell area conversely strongly increases. This area of the cell is thus more strongly loaded during flooding, which can lead to increased degradation over a longer period of time. Inhomogeneous current distribution during flooding also has a short-term impact on MEA performance: the power density of the cell decreases from 113 mW/cm^2 before flooding (Fig. 115a, top) to 78 mW/cm^2 during flooding (Fig. 115b, bottom).

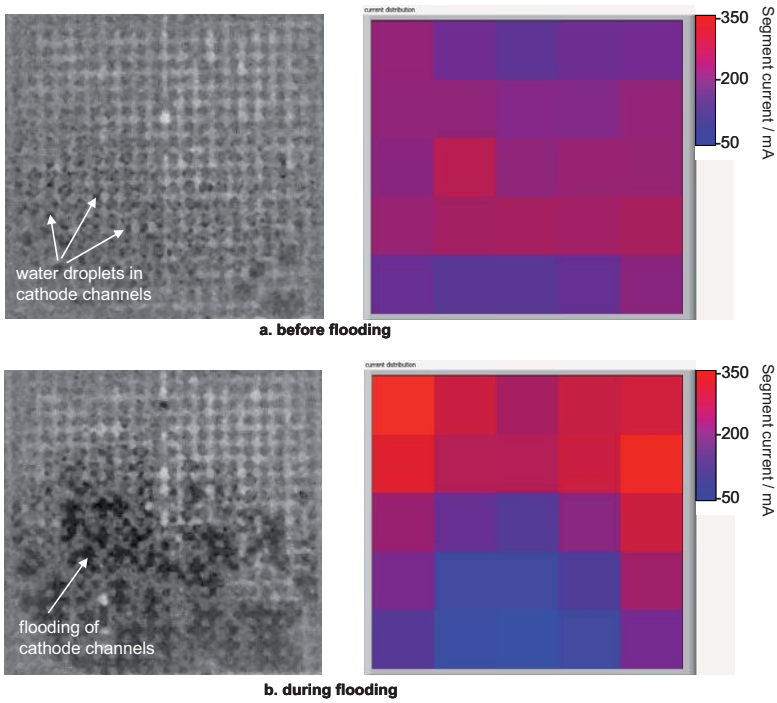


Fig. 115: **(a) Cell before flooding, (b) cell during flooding (left), normalized neutron radiogram (right): current distributions; temperature 70 °C, current density: 300 mA cm^{-2}, $\lambda_{methanol} = \lambda_{air} = 4$, flow field plates: grid geometry**

On the basis of increasing water vapor partial pressure in the air flowing through, water droplets usually form in the channels of the flow field plates in the lower and middle cell sections. The accumulation of water in these areas is favored by gravitation. An exception to this is bifunctional operation and is shown in Fig. 116. Here, for small current loads, the methanol and water supply is increased so strongly that the high water and methanol permeation causes the oxygen concentration near the air outlet, i.e. in the bottom part of the cathode, to return to zero. The oxygen depletion at the cathode leads to a current reversal in the bottom of the cell (electrolysis regime), in other words instead of oxygen reduction at the cathode, methanol oxidation occurs and the protons that are formed permeate through the membrane to the anode where they are reduced while hydrogen forms. The current reversal in the electrolysis regime can be seen clearly in Fig. 116 (right) in the form of green-colored segments. As no water is formed in the bottom part of the cathode, no water droplets are visible here in the corresponding neutron radiogram (Fig. 116, left). In contrast, in the top part of the cell, “normal” electrode reactions occur in the DMFC – i.e. methanol oxidation at the anode and oxygen reduction and water formation at the cathode (galvanic regime). For this reason, the water droplets are formed in the upper area of the cell (Fig. 116, left).

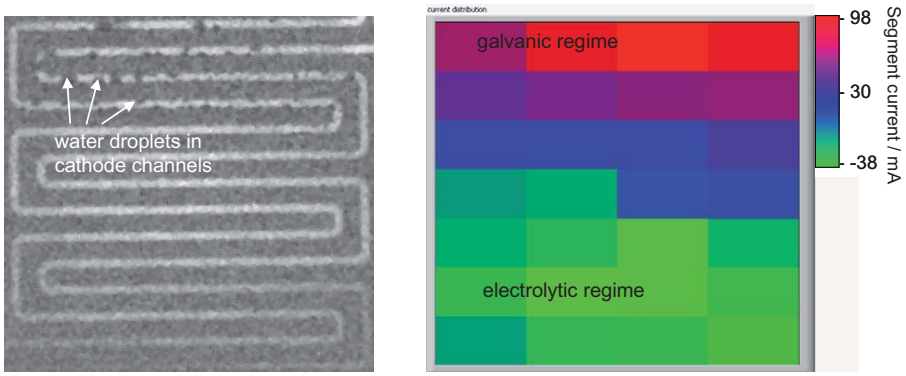


Fig. 116: Bifunctional operation (left): normalized neutron radiogram (right): current distribution; temperature: 70 °C, current density: 10 mAcm^{-2}, $\lambda_{methanol}$ = 141, λ_{air} = 6, flow field plates: double meander geometry

Both examples show that the results of current distribution and neutron radiography correlate well. However, there is no simple relationship between the corresponding gray values of the channels, on the one hand, and the segment currents, on the other. This depends on the overlapping of anode and cathode effects and also on the water management in gas diffusion layers. The separation of anode and cathode effects using neutron radiography can be achieved by means of different flow field plates at both electrodes, for example, a meander structure on the anode side and a channel structure on the cathode side (see Section 3.6.2.2), as is the case for stack cells. Another step for adapting the procedure of combined neutron radiography and current distribution measurements to the design of stack cells involves increasing the electrode area from 18 cm² to more than 300 cm². The water management in the gas diffusion layers should not only be analyzed with neutron radiography but also with synchrotron radiography in order to allow the local formation and dissolution of water droplets in the gas diffusion layers to be monitored.

4.1.5 Staff members and fields of activity

Name	Tel. (+49 2461-61-) E-mail address	Field of activity
Dr. K. Wippermann	2572 k.wippermann@fz-juelich.de	Head of the RuNPEM subproject, clarification of physical and chemical degradation mechanisms, spatially resolved measurements
A. Schröder	1579 a.schroeder@fz-juelich.de	Studies on media and current distribution in the DMFC using electrochemical, neutron-radiographic and X-ray-based techniques

4.2 Contributions for increasing reliability – The SOFC in long term tests

4.2.1 Project objectives and approach

The EU Integrated Project “Real-SOFC” aims to improve our understanding of degradation in SOFC stacks and to extend the durability of planar SOFC stacks to operating periode that are suitable for stationary applications. As part of the Real-SOFC project, three generations of SOFC stacks in the so-called F design, each with two or four planar anode-supported cells, were operated for durations of 3000 h up to 10,000 h under varying fuel and electrical load conditions.

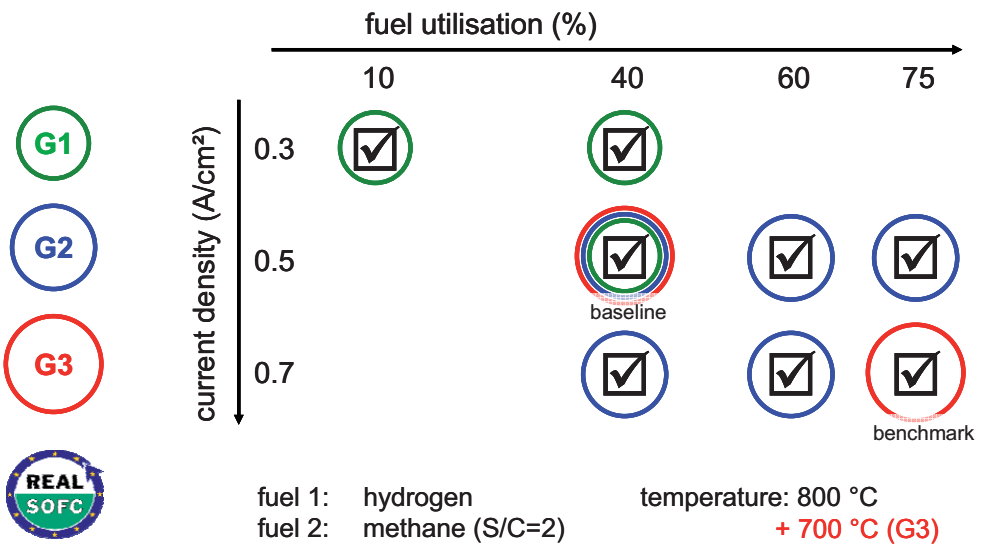


Fig. 117: The sensitivity matrix; durability tests performed on three generations of stacks in dependence on current density, fuel utilization and temperature

Standard anode substrate type cells with double-layer LSM cathodes were used in stacks of the first and second generation. The result of a first “feedback loop” was that IT11 steel from Plansee AG (Reutte, Austria), a Real SOFC partner, was used in the second-generation stacks for the interconnect plates and cell frames (this meant that the glass ceramic sealing also had to be modified). In the third-generation stacks, the results from the second “feedback loop” were used: cells with high-performance LSCF cathodes developed at Jülich (because of which, the cathode contact layer also had to be adapted). The durability tests on these short stacks were conducted at 800 and 700 °C in dependence on current density (0.3, 0.5 and 0.7 A cm^{-2}), fuel composition (hydrogen: H_2 + 3…10 % H_2O or methane: CH_4/H_2O (S/C=2)), and fuel utilization (8, 40, 60 or 75 %). The sensitivity matrix is shown in Fig. 117.

4.2.2 Test results

Fig. 118 shows as an example the results of the durability tests conducted on two first-generation stacks and two second-generation stacks. All four were operated on hydrogen with a fuel utilization of 40 % at a temperature of 800 °C. The two first-generation stacks

were operated at the current densities of 0.3 (blue/cyan curves) and 0.5 A cm^{-2} (olive/green curves), respectively. The two second-generation stacks were operated at 0.5 (purple/pink curves) and 0.7 A cm^{-2} (red/orange curves), respectively.

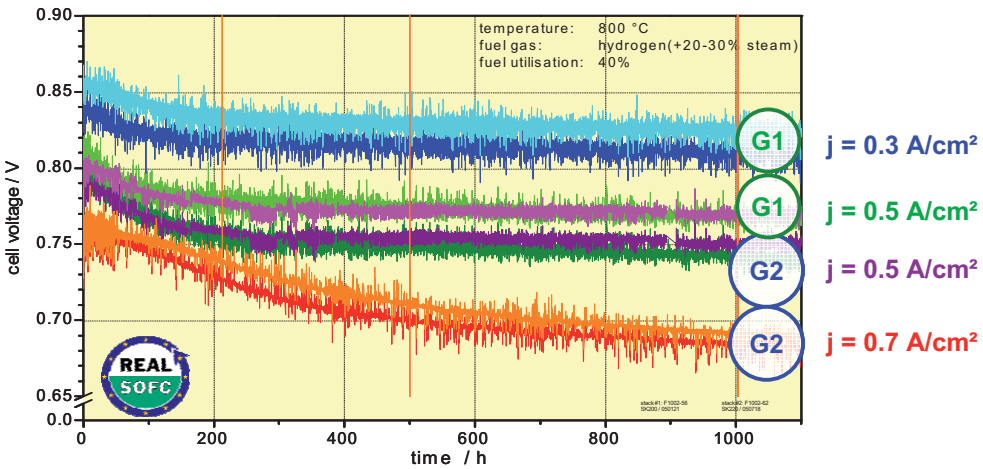


Fig. 118: Durability tests on first- and second-generation short stacks operated on hydrogen with a fuel utilization of 40 % at 800 °C in dependence on current density

For all four short stacks, the cell voltages show a large drop in performance (30…60 mV) during the initial 300…500 h of operation. This drop is more pronounced in the cell voltages of stacks operated at higher current densities. This initial drop is typical of all Jülich short stacks manufactured with similar materials for the components in the F design. After this initial period, the voltage decrease becomes quasi-linear over time. For the first-generation short stack operated at a low current density of 0.3 A cm^{-2}, this quasi-linear behavior was observed over the full 3000 h of operation. For the other three short stacks operated at higher current densities, this period of quasi-linear behavior was, however, much shorter. After about 800 to 2000 h, a deviation from linearity was observed. From this time on, the drop in voltage increased progressively with time. When the first- and second-generation stacks both operated at the same current density of 0.5 A cm^{-2} were compared, it was revealed that the period of quasi-linear behavior was longer for the second-generation short stack.

Performance tests on the first two candidate third-generation short stacks showed excellent performance due to the LSCF cathodes: under standard Real-SOFC conditions for current-density-voltage measurements, the ASR of all cells was about 0.26 Ω cm^2 at 700 °C. This is the same value as was obtained for both first- and second-generation short stacks at 800 °C. It was therefore decided to perform the durability tests on these candidate third-generation short stacks under standard baseline conditions at 700 °C, thus operating the short stacks at a similar voltage and power density. The durability tests on both candidate third-generation short stacks successfully surpassed 3000 h, at which time the stack with the ITM interconnect plates was selected as a third-generation (G3) stack. Due to its excellent

performance, it was also decided to continue the durability test on the remaining candidate third-generation short stack with the CroFer22APU interconnect plates (G3-TK).

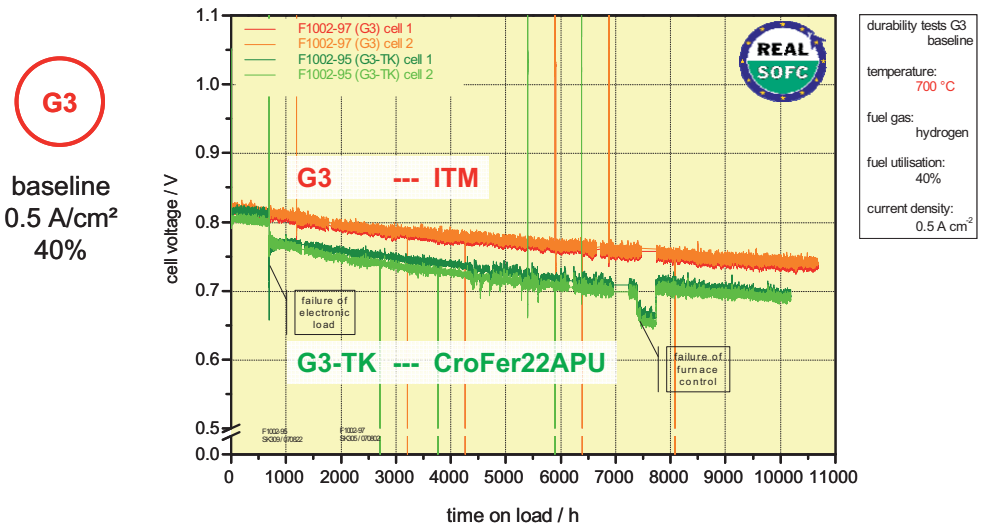


Fig. 119: Durability tests on third-generation short stacks G3 and G3-TK operated at 700 °C with hydrogen (u_F = 40 %) at 0.5 A cm^{-2}

Fig. 119 shows the results of durability tests conducted on the third-generation stacks run on hydrogen with a fuel utilization of 40 %, a current density of 0.5 A cm^{-2}, and a temperature of 700 °C. These two stacks were successfully operated for 10,000 hours, and the tests are currently being continued. The drop in performance at about 700 h for the G3-TK stack was caused by a failure of the electronic load. Between 7400 h and 7700 h, a failure of the furnace control caused a drop in the operating temperature of the G3-TK stack, which was thereafter corrected.

The first noteworthy observation was the absence of a large drop in performance in the initial 300 to 500 h of operation. This can be explained by the lower operating temperature, by the LSCF cathode or by the changed composition or increased thickness of the cathode contact layer. The second noteworthy observation was the absence – so far – of progressive degradation. Over the full period of operation, a quasi-linear degradation was still observed.

The durability tests over at least 3000 h on short stacks in dependence on the operating conditions (fuel composition, fuel utilization and current density) led to the following observations. The degradation behavior of the short stacks is not influenced by the choice of fuel (hydrogen or methane) and is hardly influenced by fuel utilization in the range of 8…75 %.

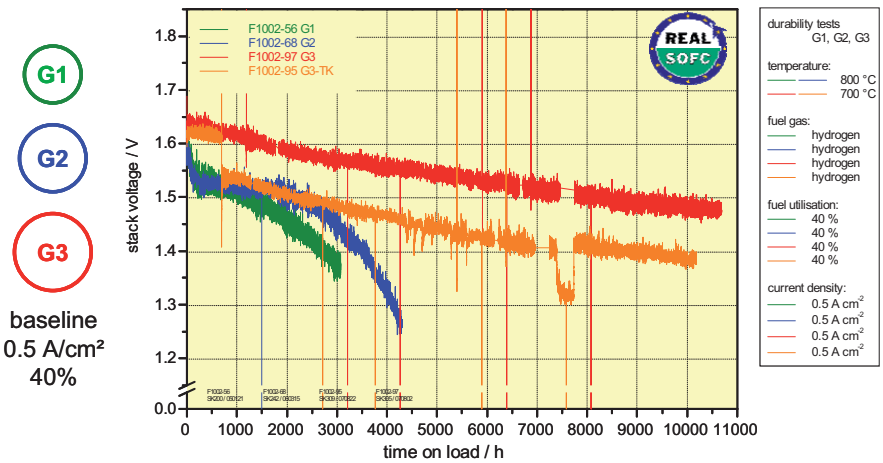


Fig. 120: Comparison of the durability tests performed on the three generations of short stacks G1 (green), G2 (blue), G3 (red) and G3-TK (orange) operated at standard baseline conditions (hydrogen, 40 % utilization, 0.5 A cm^{-2}). Note the difference in operating temperature: 800 °C (G1 and G2); 700 °C (G3)

Fig. 120 compares the results of the durability tests for all three generations of short stacks at standard baseline conditions (hydrogen, 40 % utilization, 0.5 A cm^{-2}). The degradation rates determined over the first 3000 h for the third-generation stack operated at 0.5 A cm^{-2} are much lower than those determined for the first- and second-generation stacks operated at the same current density. This is mainly due to the absence of the initial drop in performance during the first 300…500 hours of operation. The lowest degradation rates of about 20 mΩ cm^2 kh^{-1} were determined in tests on a short stack using cells with LSM cathodes operated at 800 °C with a current density of 0.3 A cm^{-2} and on a short stack using cells with LSCF cathodes operated at 700 °C with a current density of 0.5 A cm^{-2}.

The observed durability behavior of the three generations of stacks can generally be divided into four different types, as shown in Fig. 121. For the first- and second-generation stacks, an initial drop was observed in the first 300…500 h of operation. This initial drop is strongly dependent on current density. The G1 stacks operated at the lower current density of 0.3 A cm^{-2} showed a linear behavior during the remainder of operation up to 3000 h (type A). The G1 and G2 stacks operated at the higher current densities of 0.5 and 0.7 A cm^{-2} show only a relatively short period of linear behavior, depending again on current density, before the degradation behavior becomes progressive in time (type B). For the third-generation stacks, the initial drop was absent under all conditions investigated. The G3 stacks operated at the lower temperature of 700 °C showed a linear behavior over the full duration even up to 10,500 h (type C). The progressive degradation that was often found in the G1 and G2 stacks was also observed in the G3 stack that was operated at the higher temperature of 800 °C, albeit after a certain period of linear behavior (type D).

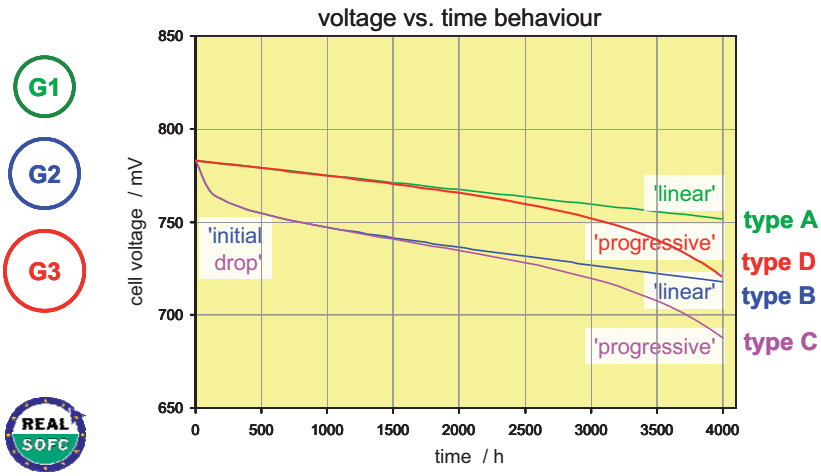


Fig. 121: Types of degradation behavior observed for the durability tests in the sensitivity analysis

Post-test characterizations of the cathodes in cells from first- and second-generation stacks showed that chromium (from the interconnect oxide layer) and copper (from the cathode contact layer) had moved into the cathode, where they were reduced and converted to a spinel phase composed of Cr, Cu and Mn at the electrolyte-cathode interface (no La or Sr was part of the spinel phase). Changes in the microstructure of the cathode in the region near the electrolyte interface were observed for all samples. This will have a significant effect on the non-ohmic polarization resistance at the electrolyte-cathode interface. However, no clear relationship could be established between the degradation rates of the stacks and the amount of Cr contained in the cathode. This observation is an argument against a connection between the Cr poisoning of the cathode and the initial drop in performance in the first time domain, because this initial drop depends heavily on current density. The absence of the initial drop in the third-generation stacks composed of cells with LSCF cathodes speaks for a connection between the Cr poisoning of the cathode and the first time domain, as LSCF cathodes are known to act as Cr getters, forming an (Sr,Cr) oxide at the interface between the cathode and the cathode contact layer before reaching the cathode-electrolyte interface.

The interpretation of the observations will remain speculative as long as no additional detailed results are available. The linear degradation behavior observed mainly in the type A and type C curves could be associated with a steady increase in ohmic resistances in the bulk layers and at interfaces, due for example to oxide scale growth, coarsening in the various layers, and (non-electrochemical) reactions at interfaces. The situation will worsen, for example, when coarsening or even spallation will lead to local contact losses at interfaces. Around the spots where contact is lost, the local current density will increase, raising the local temperature and accelerating the processes responsible for the initial coarsening and/or spallation. This successive occurrence of events may give rise to the progressive degradation observed in the third time domain of the type B and type D degradation behavior. A similar type of degradation behavior was observed previously in PEM fuel cells and was modeled by Kulikovsky *et al*.

4.3 The use of mineral oil products in fuel cells – The desulfurization of middle distillates

4.3.1 Challenges and choice of procedure

In order to operate fuel cells with the middle distillates available on board aircraft, ships and heavy goods vehicles, the fuel must first be converted into a hydrogen-rich gas by a catalytic reforming process. The Institute of Energy Research – Fuel Cells (IEF-3) at Forschungszentrum Jülich GmbH is currently working in close cooperation with companies from the aviation industry on fuel cell systems that use kerosene as an energy carrier. Other cooperations are planned for the automobile sector and for the shipping industry. Since the catalysts both in the reformer as well as in the fuel cell are deactivated by the sulfur compounds contained in different types of fuel, the fuel must be desulfurized before it is reformed.

Whereas diesel fuel for road vehicles within the EU is desulfurized at the refinery, globally kerosene is permitted to have up to 3000 ppm sulfur, and bunker gas oil for fuelling vessels on inland waterways may contain up to 1000 ppm sulfur in the EU. As hydrodesulfurization used in refineries is not suitable for mobile applications, new processes must be developed and tested.

In a completed PhD thesis, a large number of processes were experimentally tested and evaluated in terms of their suitability as a component in a multistage desulfurization process in fuel cell systems for mobile applications. Four processes were identified as candidates: the thermal separation of high-boiling kerosene fractions with high sulfur concentrations, pervaporation with membranes, the adsorption of sulfur-containing components in fuel, and hydrodesulfurization with presaturation. In laboratory experiments, it was demonstrated that adsorption in combination with either thermal separation or pervaporation with membranes is suitable for the desulfurization of kerosene. From an economic point of view, combining adsorption and thermal separation is generally disadvantageous, as this process was shown to have a comparably high energy demand. Hydrodesulfurization with presaturation also provided very promising results on a laboratory scale. This process was also verified by experiments on a scale of 5 kW_{el}.

4.3.2 Promising processes and their performance

In this section, the results of two types of experiments are discussed: (i) experiments on hydrodesulfurization with presaturation, and (ii) experiments conducted on a combined process of pervaporation and adsorption. Both processes were evaluated using a process analysis approach in combination with application in aircraft. The results discussed here are valid for the desulfurization of kerosene.

4.3.2.1 Hydrodesulfurization with presaturation

This process involves dissolving a sufficient amount of hydrogen in kerosene in order to be able to convert all of the sulfur present in the kerosene in a bound form in complex aromatic compounds. The quantity of hydrogen that can be dissolved in the kerosene is proportional to the overall pressure and can be calculated according to Henry's law.

In order to investigate the influence of different fuel qualities on the composition of the product of hydrogenation with presaturation, four different kerosene qualities were investigated and compared on a laboratory scale. The results of these experiments are shown in Fig. 122.

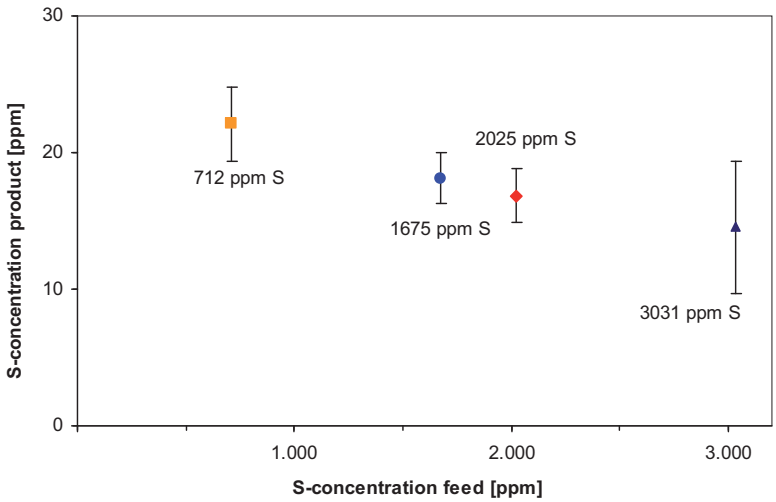


Fig. 122: Dependence of the sulfur concentration in the product on the initial concentration of sulfur in kerosene, T = 390 °C, p = 70 bar, LHSV = 0.7 h^{-1}

For all four different kerosene qualities, the sulfur concentration in the product was in the range of 10 to 25 ppm. The observation that the sulfur concentration in the product drops with rising sulfur content in the initial fuel can be explained by the fact that different types of sulfur compounds are present in the different initial fuels. The results show that hydrodesulfurization with presaturation has the potential to achieve the target value of 10 ppm sulfur in the product. However, further improvements to the process are required to achieve this. There is no need for an additional desulfurization step.

Another experiment was performed with a pilot plant in order to demonstrate the technical concept for H_2S separation, to scale up the experimental data, and to demonstrate the technical relevance of the process. The pilot plant can process mass flows of kerosene which lead to an electric power of approx. 5 kW in a fuel cell system. The kerosene used was Jet A-1 with 712 ppm S. The experiment was performed for almost 200 h, and 382 l of kerosene were desulfurized. The H_2S was removed from the product with a nitrogen volume flow of 50 – 150 Ndm^3 / kg kerosene. The result of this experiment can be seen in Fig. 123.

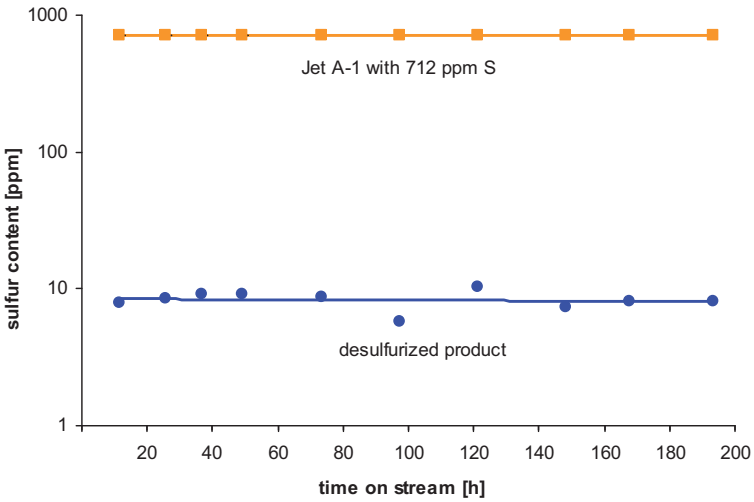


Fig. 123: Sulfur concentration of the initial kerosene and of the product after removal of H_2S

For the full duration, the total sulfur content in the product amounted to between 5.7 ppm and 10.3 ppm. A determination of the individual sulfur components in the product revealed that more than 50 % of the sulfur was present in the form of hydrogen sulfide. This demonstrated that the removal of the hydrogen sulfide by sweeping the product with a nitrogen flow of 50 – 150 l_N/h was sufficient to achieve the target value of 10 ppm sulfur in the product under the given experimental conditions.

With respect to the targets for expenditure of energy, construction volume and lifetime, hydrodesulfurization with presaturation can be evaluated as follows:

- The dimensions of the desulfurization unit were estimated to be three times the tank volume. A volume of pre-saturator and separator of 1 liter each leads to a volume of 13.2 l for the overall system.
- Although hydrodesulfurization requires high operating temperatures and pressures, only a relatively low expenditure of energy is necessary. For kerosene with 3000 ppm S, desulfurization leads to a 1 % reduction in the system efficiency of the fuel cell APU. If Jet A-1 with a sulfur content typical of the EU is used, then the efficiency of the APU is reduced by only 0.85 %.

From the points listed above, it can be concluded that according to the present state of the art, the use of hydrodesulfurization with presaturation involves acceptable efforts for process optimization with a view to technical applications.

4.3.2.2 Desulfurization of kerosene by a combined procedure of pervaporation and adsorption

As part of a comparative study, different membranes were examined using the Jet A-1 fuel with 564 ppm S. Fig. 124 shows the enrichment factors as a function of the transmembrane flow for the various membranes.

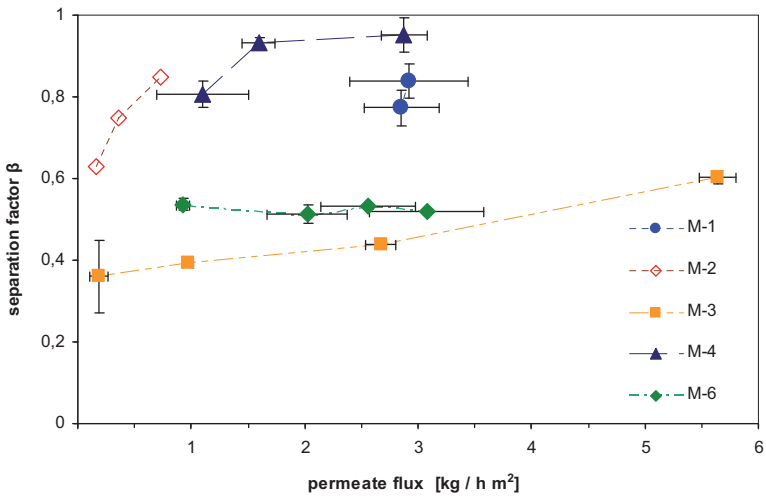


Fig. 124: Separation factors and permeate fluxes in the membranes examined with the Jet A-1 fuel A at $T_{permeate}$ = -196 °C

With membrane M-1, which is used industrially for pervaporation, the sulfur in the permeate was depleted by about 16 to 23 %. With membrane M-2, which is selective for aromatic compounds, the sulfur content in the permeate was also depleted. Due to the polymer used, the operating temperature of the membrane could not exceed a limit of 110 °C. Since, however, the sulfur compounds were over-proportionally contained in the high-boiling range of the kerosene, this temperature was insufficient to achieve enrichment of the sulfur content in the permeate. The results with membrane M-4, which was also designed for the enrichment of aromatic compounds, confirm the conclusion that the low vapor pressure of the high-boiling sulfur compounds counteracts the enrichment of aromatics in the permeate. The observed enrichment factors ranged from 0.81 to 1.05. Consequently, the membrane is not suitable for the desulfurization of kerosene. Although membrane M-3 is defined as a membrane selective for aromatic compounds according to its patent, the experiments yielded enrichment factors of between $\beta = 0.36$ and $\beta = 0.6$. For operating points with enrichment factors of less than 0.4, the transmembrane flux was more than 1 kg/h m^2, and with an enrichment factor of 0.6, it achieved rates of up to 5.64 kg/h m^2. The membrane thus demonstrated the best results for depletion of the sulfur content in the permeate. Membrane M-6 can also be regarded as a promising candidate. The separation factor was approximately 0.5 at permeate fluxes of 0.93 – 3.08 kg/h m^2.

The experiments on adsorption were performed on a laboratory scale at atmospheric pressure in a fixed-bed reactor. In a detailed screening, ten different commercial and newly developed adsorbents were examined with respect to their adsorptive capacity, stability, and ability to regenerate.

Fig. 125 shows the adsorption behavior of the four most active adsorbents. For these experiments, the 50 % light fraction of Jet A-1 fuel (564 ppm S) was used, which still displayed 290 ppm S. The curve was determined for the accumulated sulfur content in the product. To this end, the adsorbents were regenerated several times and used for

adsorption. The experiments were repeated until a stable adsorption capacity had been established.

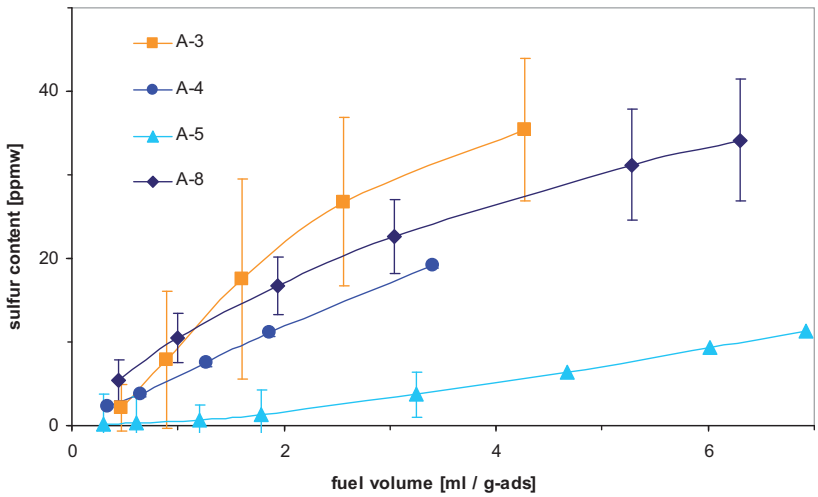


Fig. 125: Screening of adsorbents with 50 % light fraction from Jet A-1 (564 ppm S), cumulative breakthrough curves, recorded in consecutive desulfurization cycles

The highest adsorption capacity of the equivalent of 1.52 mg S / g adsorbent was obtained with the material A-5. The adsorption capacity of the remaining adsorbents was more than 76 % smaller. As a result, it was decided to continue to use adsorbent A-5 in the subsequent experiments.

Fig. 126 shows the influence of different reaction conditions for the regeneration of adsorbent A-5 on the course of the cumulative breakthrough curves. Such conditions are the regeneration temperature T_{reg}, the time t at which the adsorbent remains at T_{reg}, and the GHSV of the regeneration medium air. Under the initial regeneration conditions (T_{reg} = 200 °C, t = 2 h, GHSV = 655 h^{-1}), it was possible to treat 2 ml of fuel / g kerosene until the cumulative sulfur content in the product showed a limit of 10 ppm S. Under optimum regeneration conditions (Treg = 500 °C, t = 3 h, GHSV = 655 h^{-1}), the corresponding value was 6.4 ml. The adsorbent A-5 was fully cyclically regenerated under these conditions. An alternative to the optimum conditions are the economic conditions (Treg = 450 °C, t = 2 h, GHSV = 200 h^{-1}). A lower expenditure of energy and a lower quantity of regeneration medium are necessary to establish these conditions. Furthermore, lower demands are made on the materials required for the regeneration reactor, and the tendency of the adsorbent to undergo sintering is reduced. Under economic conditions, the breakthrough capacity of adsorbent A-5, however, is reduced by 20 %.

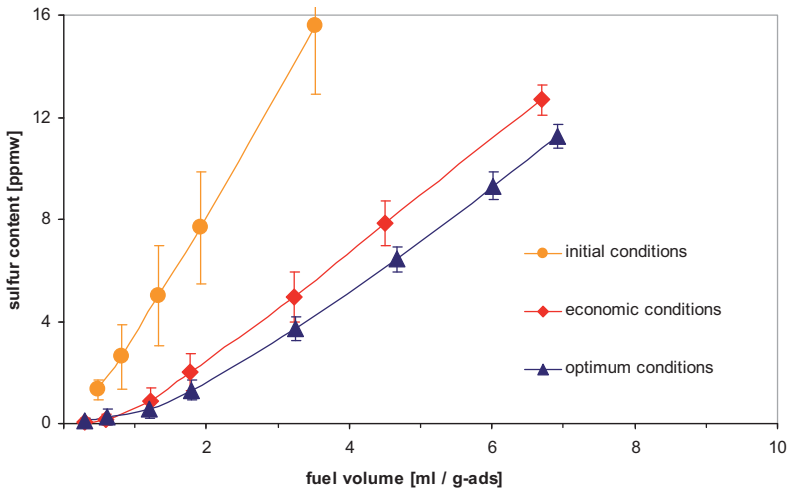


Fig. 126: **Development of the adsorption capacity of adsorbent A-5 by optimizing the regeneration process, T_{ads} = 20 °C, LHSV = 1 h^{-1}, 50 % light fraction of Jet A-1 (564 ppm S); initial conditions: T_{reg} = 200 °C, t = 2 h, GHSV = 655 h^{-1}; economic conditions: T_{reg} = 450 °C, t = 2 h, GHSV = 200 h^{-1}; optimum conditions: T_{reg} = 500 °C, t = 3 h, GHSV = 655 h^{-1}**

The volumes in Tab. 4. were obtained for a 5 $kW_{el.}$ fuel cell system for the dimensions of a desulfurization unit consisting of one or two hollow-fiber modules for pervaporation and a fixed-bed reactor for adsorption.

Volumes in liters	Holow-fiber module	Adsorbent	Total
Single-stage, with recycling	1.26	10.00	33.78
Two-stage, with recycling		4.38	23.28
Stage 1	2.09		
Stage 2	1.29		
Single-stage, without recycling	1.21	8.36	28.71
Two-stage, without recycling		3.75	21.09
Stage 1	2.03		
Stage 2	1.25		

Tab. 4: **Volume of unit for desulfurization by pervaporation and adsorption, designed for kerosene with 3,000 ppm S**

In Tab. 4, the term “recycling” is taken to mean that part of the retentate from the pervaporation is recycled in order to reduce the quantity of fuel that must be added. In a two-stage pervaporation process, the low-sulfur permeate from the first stage is separated in the second stage into a sulfur-enriched permeate and a low-sulfur retentate. The full dimensions of the desulfurization unit were once again estimated to be three times the tank volume of a hollow-fiber module and a fixed-bed reactor for adsorption. This estimate for the various process concepts shows that although two-stage pervaporation requires an additional hollow-fiber module, it has advantages over the single-stage process because of the reduced quantity of adsorbent required. The design without recycling also requires smaller volumes because a smaller quantity of adsorbent is required.

The performance loss during the two-stage pervaporation process with recycling amounts to 3.1 % when the APU is run on kerosene containing 3,000 ppm S. If the desulfurization unit designed for 3,000 ppm S is operated with Jet A-1 containing 564 ppm S (a typical sulfur content for Europe), then the performance loss only amounts to 0.7 %.

4.3.3 Outlook for the next few stages of R&D

There is a great need for research and development on membrane materials for the process involving pervaporation with membranes. The contact between the fuel and the membrane can – depending on the membrane material – lead to an enrichment or a depletion of the sulfur concentration in the permeate, in other words, to the mass flow which diffuses through the membrane or dissolves within it. The targets for development are good enrichment or depletion factors, high flows through the membrane, and a sufficient mechanical and thermal stability of the membrane material for technical applications. In polyimide membranes, for example, the manner in which the individual organic substances are combined in the membrane as well as the degree of the connectivity between the individual polymer strands are decisive for setting these targets. In a research cooperation with the University of Düsseldorf, it is planned to synthesize and test membrane materials in Jülich. Commercial membranes are also to be analyzed in terms of the targets mentioned above. If suitable materials are available, a hollow-fiber module will be designed, constructed and tested for technically relevant mass flows in the kW range.

The permeate, in other words the kerosene flow after it has permeated the pervaporation membrane, does not contain any more dibenzothiophene but it still contains significant amounts of alkylated thiophene, as well as mono-, bi- and tri-alkylated benzothiophene. These materials are in a kerosene matrix, in other words a multicomponent mixture of different hydrocarbon classes. The materials for adsorbing these substances must be improved further. The most important suitability criteria include adsorption capacity and the regenerability of the materials. The regeneration must occur in the fuel cell system with as little effort as possible. Additional media, such as pure hydrogen or pure oxygen, cannot be produced in the system. These activities will be pursued in cooperation with the Institute for Industrial Chemistry at the University of Stuttgart.

Building on these new developments and knowledge, the combination of adsorption and pervaporation will be designed anew, verified in experiments, and evaluated. Analyzing this combination on a kW scale is another aim.

As outlined previously, hydrodesulfurization with presaturation has already been successfully demonstrated on a scale of 5 $kW_{el.}$ for kerosene. More than 200 l of desulfurized kerosene

were produced. The substep of hydrodesulfurization was performed on a freely available, commercial catalyst that was not specially developed for this particular application. There is significant room for improvement here. This potential will be determined experimentally.

4.4 Zero-CO_2 use of fossil energy carriers – Optimized process for integrating CO_2 separation into the power plant process

Around 50 % of global warming can be attributed to anthropogenically produced CO_2. Avoiding CO_2 emissions by means of carbon capture and storage (CCS) was first implemented in the Norwegian SLEIPNER project (Fig. 127). CO_2 produced during natural gas extraction in the North Sea has been pumped into a saline aquifer for more than 10 years. CO_2 with a high purity of 93 – 96 mol % is separated from this natural gas. This ensures that losses in terms of compressibility are kept at an acceptable level, as suitable storage volume is limited worldwide.

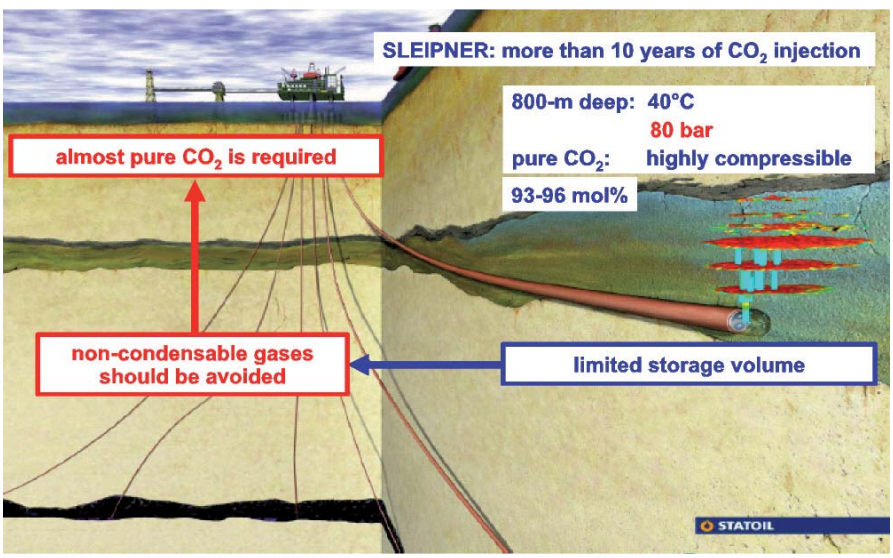


Fig. 127: For storage, two major requirements must be fulfilled by the CO_2: high purity and high pressure

The largest CO_2 point sources in the world are mainly coal power plants. This is the reason why one of the main objectives is to develop suitable processes for separating CO_2 out of power plants. The most obvious process involves CO_2 separation in the flue gas (post-combustion capture). A number of new power plant processes are emerging that would make little sense without CO_2 separation. In these power plants, separation consists of separating O_2 from air (oxyfuel process) and CO_2 or H_2 from what is known as shifted coal gas (pre-combustion capture in IGCC with additional CO shift). Work has already begun on a large number of projects with a narrow spectrum of conventional separation techniques (amine washing, cryogenic air separation and physical scrubbing). It would appear unlikely that the additional energy expenditure required for these separation technologies can be decreased to a satisfactory level. The reputation of alternative separation processes is growing. There are great expectations for the further development of membrane technology and its integration in the power plant technology (of the future).

For Forschungszentrum Jülich's own project entitled "CO_2 Separation" and the BMWi-funded projects METPORE (post-combustion) and OXYMEM, as well as the HGF MEMBRAIN

Alliance, process analyses were conducted at IEF-3 on future membrane power plants running on coal. The following questions were addressed:

- What membrane selectivity is required in each case?
- Are CO_2 impurities caused by the membrane, the power plant or both?
- Can the low-energy membrane separation processes be used in power plants that have been modified for conventional separation processes?
- What prospects are there for achieving "zero-energy" membrane operating conditions by further modifying power plants (specially designing them for membranes!), in other words without the use of extra turbomachines (2^{nd} generation of membrane power plants according to IEF-3's definition)?

The oxyfuel and pre-combustion power plant classes, in particular, were expanded with new variations. With regard to oxyfuel, by forgoing the air pressure mode in the OXYVAC-JÜL concept, there is a good chance of making the membrane module a reality in the medium term and of significantly simplifying the process membrane environment. A completely new approach known as IGSWEEP-JÜL was developed for coal gasification power plants (IGCC). This process involves an IGCC specially designed for the H_2 membrane, in which a membrane-compatible N_2 sweep gas is produced, which in turn enhances the membrane and makes "zero-energy" operating conditions possible. In other words, it allows turbomachines to be excluded from the membrane environment for the first time.

4.4.1 Challenges and choice of procedure

For a globally successful CCS, there are two requirements that appear essential today:

- high CO_2 purity (pipeline transport, limited storage volume)
- low efficiency losses (increased demand for coal, power losses)

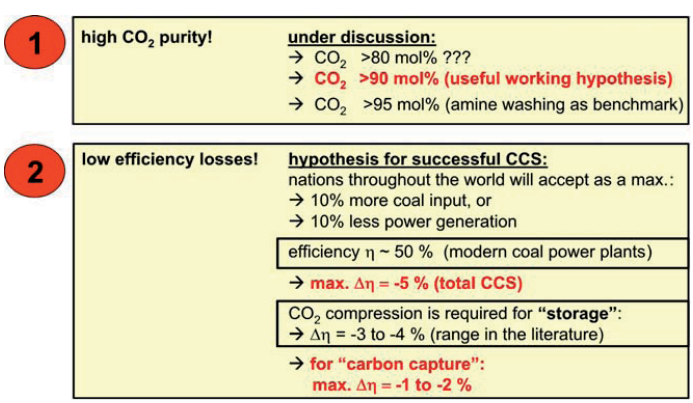


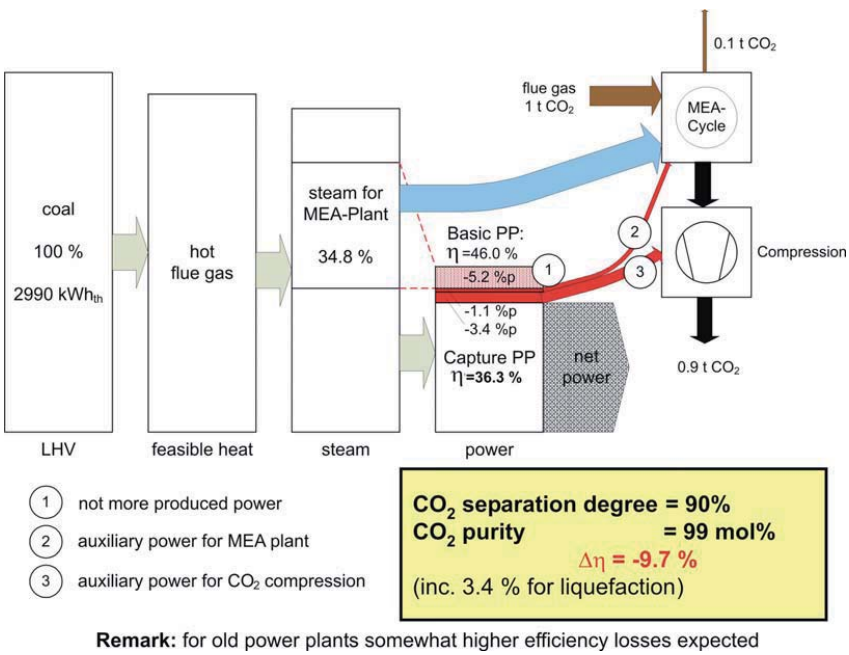
Fig. 128: Main criteria for a globally acceptable CO_2 separation technology

Fig. 128 quantifies and summarizes these requirements. The evaluation and development of concepts in IEF-3 today are based on the following working hypotheses:

- minimum value for CO_2 purity: 90 mol%
- maximum value for increased coal demand: 10 % relative, which gives rise to:

- maximum value for efficiency losses: 5 % for the complete CCS process
- maximum value for efficiency losses: 1-2 % for the “capture” process in the power plant (the balance for CO_2 liquidification)

How difficult it will be to fulfill the energy requirements has already become clear with a post-combustion pilot power plant with amine washing (today, preferentially with the solvent monoethanolamine (MEA)). IEF-3 conducted a study on this within the framework of MEMBRAIN. Fig. 129 shows the typical high energy flows (steam and current), which are the minimum required to operate an MEA cycle including regeneration of the solvent (release of CO_2 gases). For older (refitted) power plants, steam extraction from the turbine process causes even greater efficiency losses (up to 15 % for the complete CCS process).



Remark: for old power plants somewhat higher efficiency losses expected

Fig. 129: Post-combustion with conventional CO_2 separation by amine washing (solution aqueous MEA): energy balance of the complete power plant process (reference quantity is 1 t produced CO_2 in flue gas)

A refined systematic classification of possible future power plant concepts was then performed in a two-dimensional matrix. This is valid for power plants with conventional gas separation as well as for membrane power plants. The three CO_2 separation principles (post-combustion, oxyfuel and pre-combustion) with the three gas separation purposes (CO_2/N_2, O_2/N_2 and H_2/CO_2) were applied to three basic coal power plants: steam power plants (SPP), IGCC/standard and IGCC/CO shift/H_2 turbine (Fig. 130). The “total oxy IGCC” process, in particular, which was not really considered an option in the past and now involves the combustion of coal gas with pure oxygen in addition to gasification, can be clearly seen in the middle of the matrix.

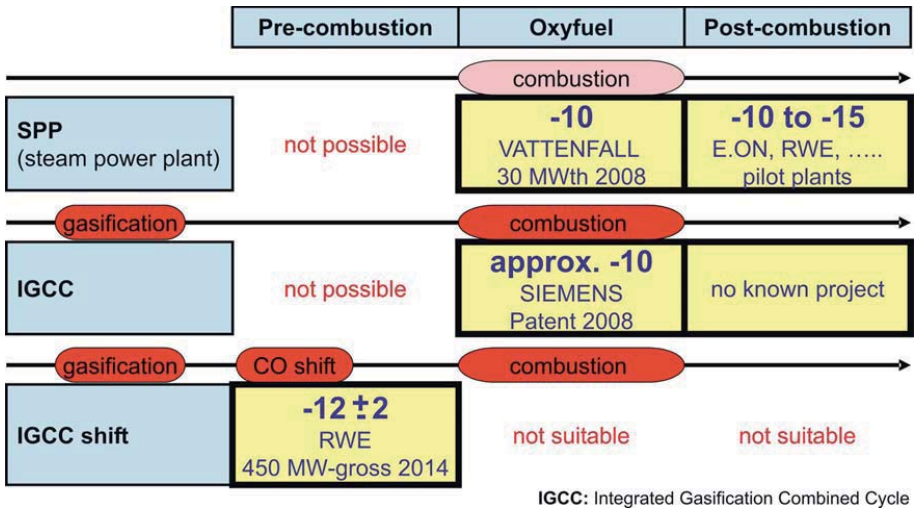


Fig. 130: Classification of future coal power plants with CO_2 separation. The 3x3 matrix shows the energy situation for current industrial projects with conventional gas separation technologies. The figures represent the expected efficiency losses in % (including CO_2 compression)

The best power plant in the distant future is expected to be among the oxyfuel processes because

- the combustion process will remain a one-stage compact process, and
- combustion with O_2 means that no N_2 will infiltrate the combustion process (dilution of CO_2 avoided).

Where conventional separation techniques are concerned, it remains questionable as to whether efficiency losses well below 10 % can be achieved (2nd generation according to the definition by E.ON). Today's studies and projects deliver efficiency losses between 10 and 15 % (Fig. 130). "Capture" (including additional preparatory measures such as adding steam for the CO shift in pre-combustion) accounts for the largest proportion.

Membranes, in contrast, at least in principle (under suitable conditions) have the potential in terms of energy to perform gas separation processes with zero energy demand (excluding flow pressure losses). In the world's largest membrane plant in Pakistan (membrane area of 0.4 km^2), for example, CO_2 is separated during the extraction of natural gas under an overall pressure of approx. 100 bar using polymer membranes, whereby high natural driving forces exist for CO_2 permeation. This allows the use of cellulose acetate membranes with high CO_2/CH_4 selectivity, despite the fact that these membranes only exhibit a low CO_2 permeability.

Although there are originally not enough natural driving forces, there is still hope that ingenious engineering measures or power plant modifications will help to achieve similarly attractive conditions for membrane application in power plants. All three gas separation techniques can in principle also be used with membranes. The membrane separation process, compared to conventional processes, can lead to both lower separation factors

(post-combustion) as well higher separation factors (oxyfuel with mixed conductor membranes).

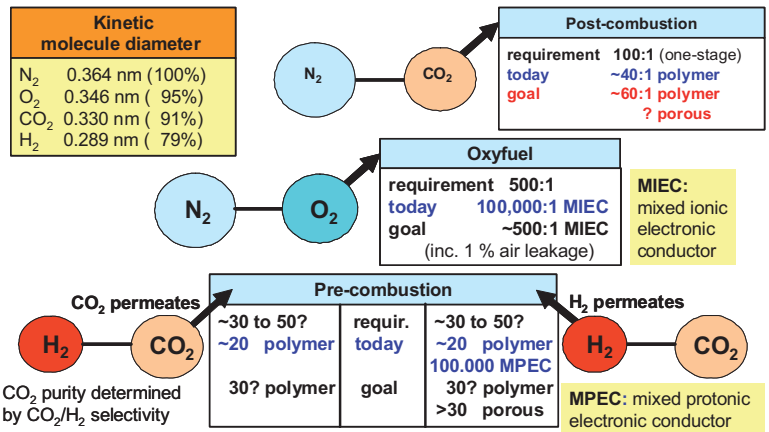


Fig. 131: Membrane selectivities: requirements – state of the art – MEMBRANE objectives (for sufficient permeability, exception: for protonic-electronic mixed conductors, only low permeabilities have been achieved to date)

The fact that the kinetic diameters of the main molecule types involved are very similar poses a huge challenge (Fig. 131). This is the reason why separation tasks will most likely only be performed with porous membranes where only low membrane selectivities are required. As this is only the case for pre-combustion, other membrane classes must also be incorporated. It is therefore advantageous that two other classes actually exist, which are characterized by separation mechanisms that are not based on the size of molecules:

- (organic) polymer membrane (separation mechanism based on solubility and diffusion) and
- ionic-electronic and protonic-electronic mixed conductors for O_2 and H_2 separation, respectively, (separation mechanism based on the generation of electrically charged species of oxygen ions and/or protons, which allows perfect selectivity, for example 100,000:1, to be achieved in defect-free membranes, which means that the selectivity of a membrane module is solely determined by the joint quality)

One result of process analyses is recommended values or standards for selectivity requirements (Fig. 131). In order to estimate the attractiveness of using a membrane and the prospects of success associated with further membrane development, these standards (Fig. 131) are compared to the membrane selectivities today and those that will be achieved in the near future (for the most suitable type of membrane in each case). In the oxyfuel process, considerable impurities, particularly from the power plant (mainly O_2 and N_2) ended up in the CO_2. This is why it is particularly important in this case to perform the O_2/N_2 separation with a very high membrane selectivity, for example 500:1, as this limits further N_2 impurities to 1 mol%.

Post-combustion makes the discrepancy between selectivity requirements and their achievability clear. In the medium term, only two-stage (cascaded) membrane arrangements

will be capable of performing the separation. In terms of energy, however, this is extremely disadvantageous, as the second membrane must also be operated with a turbomachine (compressor and/or vacuum pump). In addition, there is no suitable sweep gas on the horizon today for eliminating the turbomachine in post-combustion. Fig. 132 shows typical selectivity requirements and the membrane area required for a 1000 MW power plant as a function of the degree of CO_2 separation for CO_2 purities of 80 and 90 mol% as determined for a model flue gas containing 14 mol% CO_2 and simplified 86 mol% N_2. If we hope to achieve anything close to total CO_2 separation, then a membrane area of 10 km^2 would be necessary because of the low driving force of CO_2 permeation caused by low CO_2 partial pressure in the flue gas, which is still released in the separation process. The CO_2 flux density is of the order of 0.05 Nm^3/m^2h.

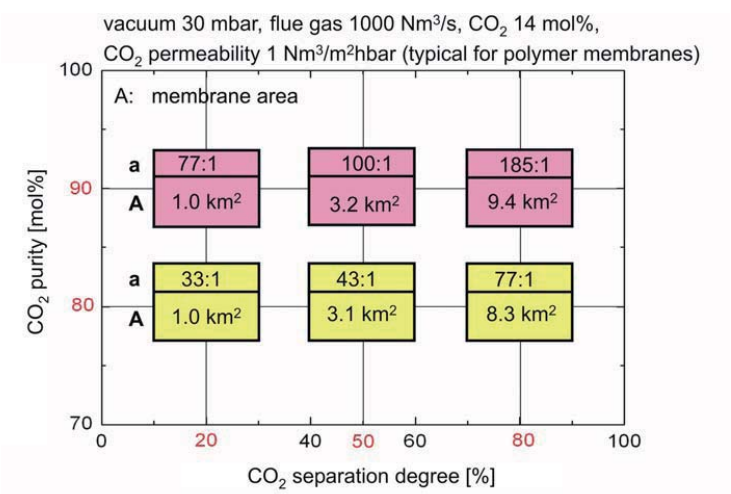


Fig. 132: Post-combustion: necessary membrane selectivities α and membrane area required for power plants of approx. 1,000 MW

Membrane power plants give rise to a third dimension in the classification as there are different measures for generating positive permeation driving forces, each of which has a very different effect on the power plant process. For example, the O_2-N_2 membrane in oxyfuel steam power plants can be operated under the following conditions (Fig. 133):

- feed gas compression (BMWi project OXYMEM)
- permeate vacuum (Forschungszentrum Jülich OXYVAC-JÜL design)
- sweep gas on the permeate side (no known project; very low driving force at the sweep gas outlet when this measure is applied alone)
- combination of these three measures, for example, in the OXYCOAL-AC concept (compression of air and recycling of the atmospheric CO_2 flue gas as a sweep gas)

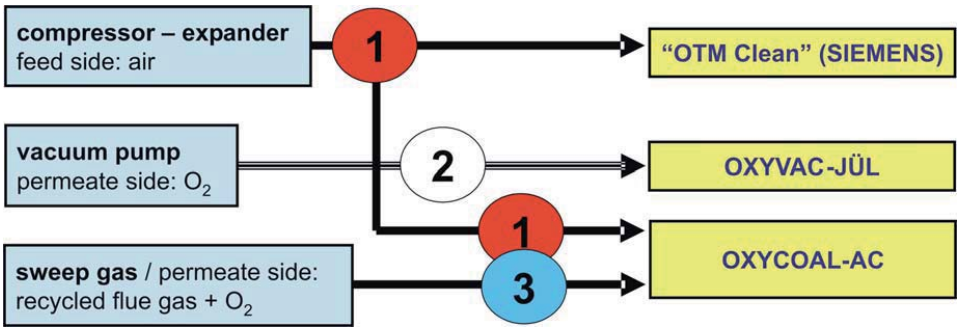


Fig. 133: Three process engineering measures can be used to create or increase the driving force for permeation. All were investigated in the oxyfuel steam power plant

4.4.2 Description of the "OXYVAC-JÜL" process concept

Oxyfuel processes are characterized by very simple CO_2 separation after combustion with pure oxygen. Combustion in pure oxygen only generates two combustion products: CO_2 and steam. Steam can be separated from CO_2 by means of condensation when the gas mixture is cooling down. VATTENFALL is developing oxyfuel power plant technology using conventional O_2 separation in air (cryogenic air separation unit, ASU). The starting point for the line of membrane power plants is the OXYCOAL-AC concept, which has been pursued for a number of years with two process engineering measures, air compression and CO_2 flue gas membrane sweeping, for the generation of high driving forces. This results in the advantage of high local O_2 partial pressure ratios of typically 20:1 (4 bar/ 0.2 bar) and higher. On the other hand, operation under pressure and flue gas membrane sweeping also has a large number of disadvantages:

- high pressure difference between the feed side and the permeate side leads to very high stability requirements for the membrane module and the high-temperature recuperative heat exchanger to preheat the air
- residual combustion products enter the permeate side of the membrane
- CO_2 atmosphere on permeate side limits the choice of membrane (barium-containing perovskite membranes exhibit the highest O_2 flux densities but have stability problems in CO_2 atmosphere)

OXYVAC-JÜL involves a new oxyfuel process which avoids all of these disadvantages (Fig. 134):

- The feed side of the O_2 membrane is operated with atmospheric air. Preheating is performed recuperatively over almost the full temperature range (typically 20 - 700 °C). Only a small amount of natural gas must be added for final preheating (700 - 800 °C; the alternative would be final preheating of air in the steam generator). Suitable membrane temperatures from the current perspective are between 700 and 1,000 °C.
- The membrane permeate side is not swept with recycled flue gas as it contains CO_2 and residual combustion products from coal combustion.

Correspondingly, the permeate side must be loaded with a vacuum in order to achieve lower O_2 partial pressures during operation on this side of the membrane than those that exist on the feed side. State-of-the-art commercial membrane technology is capable of achieving a vacuum pressure level of 50 mbar with a vacuum pump in a membrane module (according to information from BORSIG on polymer membranes). This then directs the oxygen with atmospheric pressure into the oxyfuel block.

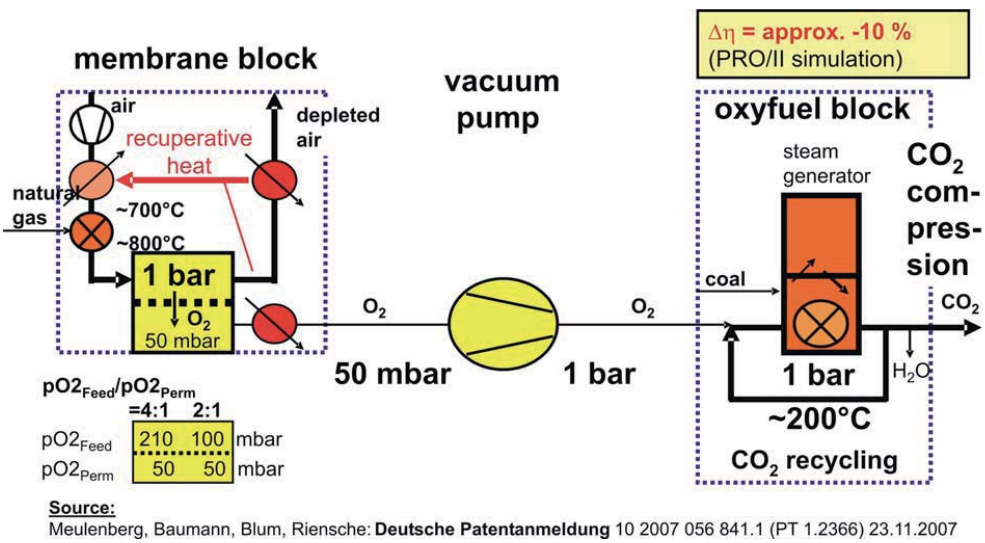


Fig. 134: OXYVAC-JÜL: generation of driving forces for O_2 permeation using a permeate vacuum. The basic variation consists of final preheating of air using natural gas firing

Compared to the OXYCOAL-AC concept, only low O_2 partial pressure ratios occur in membrane – typically between 2:1 and 4:1 (210 mbar/ 50 mbar) – which leads to adverse lower O_2 flux densities.

Preliminary measurements of the O_2 flux were performed on a barium-containing perovskite (BSCF) at IEF-1. For these measurements, the vacuum pressure of 50 mbar was simulated by approximation by setting the O_2 partial pressures to approx. 50 mbar using helium sweep gas. An O_2 flux density of approx. 1 Nm^3/m^2h was measured (approx. 5 Nm^3/m^2h for O_2 partial pressure ratios corresponding to OXYCOAL-AC). For a 1000-MW OXYVAC-JÜL power plant, this equals a membrane surface area of approx. 0.5 km^2 (approx. twenty times less than is required for post-combustion and five times greater than for OXYCOAL-AC). In Germany, around 100 GW of generating capacity have been installed. If these power plants were to be replaced by OXYVAC-JÜL power plants and the membrane area was to be related to the number of inhabitants, then we would have an O_2 membrane area requirement of approx. 0.5 m^2/inhabitant.

O_2 production is no longer physically integrated in the oxyfuel combustion process. For the development of the power plant in its entirety, this means the following:

- The O_2 membrane block can be developed separately; only the membrane module is not yet available today.

- Once the oxyfuel block has been developed, for example at VATTENFALL (initially with ASU), whereby only available power plant components are adapted to suit each other, then the components can be combined to form an OXYVAC-JÜL membrane power plant. According to preliminary simulation calculations with the PRO/II plant program, efficiency losses of approx. 10 % can be expected.

4.4.3 Description of the "IGSWEEP-JÜL" process concept

At the coal gasification power plant (IGCC), a completely new process approach was developed involving an IGCC concept that was especially adapted for the H_2 membrane, which is characterized by the following unique features:

- Air ratio reduction from approx. 3 to almost 1 gave rise to a flue gas containing very little oxygen instead of approx. 12 mol%.
- The amount of fresh air now lacking (for cooling the gas turbine burner) is replaced by recycled low-O_2 N_2 flue gas.

After the turbine compression stage (now "tandem compression" of fresh air and recycled N_2), this recycled N_2 flue gas can be fed without any diversions and without any additional energy expenditure straight into the membrane. There, a strong sweeping of the membrane permeate side takes place with this membrane-compatible pressurized gas. In this way, the driving force is created for H_2 permeation and the membrane can be integrated into the subsequent combined cycle power plant operated at high pressure without any energy-intensive H_2 recompression. There is another decisive advantage: high H_2 separation rates can be achieved because when the sweep gas enters the membrane (counter flow to feed gas), it does not yet contain H_2, while for all of the previously existing concepts with H_2 recompression, a different uniform partial pressure which is not zero was present on the permeate side, which thus critically reduced the driving force of permeation, particularly at the critical end of the H_2 separation process.

IGSWEEP-JÜL appears to be an option in the medium term, provided that

- a power plant builder develops IGCC in its modified operation mode, and
- a membrane developer adapts and improves polymer membranes, which already exhibit a very promising H_2/CO_2 selectivity of approx. 20:1 today.

For this first membrane power plant of the second generation (no compressors in the membrane environment), an efficiency loss of 7 % was calculated. For standard IGCC, an efficiency of at least 50 % is predicted in the medium term. IGSWEEP-JÜL would make an efficiency of at least 43 % possible for CCS, which corresponds to today's state-of-the-art modern steam power plants (without CO_2 separation).

4.4.4 Staff members and fields of activity

Name	Tel. (+49 2461-61-) E-mail adress	Field of activity
Prof. L. Blum	6709 l.blum@fz-juelich.de	Head of Fuel Cells Process Engineering
R. Menzer	6708 r.menzer@fz-juelich.de	Plant simulation, power plant engineering, process analyses, pre-combustion
J. Nazarko	3742 j.nazarko@fz-juelich.de	Plant simulation, power plant engineering, amine washing, oxyfuel processes
Dr. E. Riensche	6689 e.riensche@fz-juelich.de	Plant simulation, power plant engineering, CO_2 separation
Dr. Dr. L. Zhao	4064 l.zhao@fz-juelich.de	Membrane processes, plant simulation, CO_2 sequestration, post-combustion

4.4.5 Important publications and patents

Important publications

Gestel, T. van; Meulenberg, W.A.; Bram, M.; Riensche, E.; Blum, L.; Grube, Th.; Menzer, R.

Gasseparations-Membranen mit nanostrukturierten Funktionsschichten für die CO_2-Abtrennung bei Post-combustion Capture und die H_2/CO_2-Trennung bei Pre-combustion Kohlekraftwerken
(Gas separation membranes with nanostructured functional layers for CO_2 separation in post-combustion capture and H_2-CO_2 separation in pre-combustion power plants)

Der 4. Deutsche Wasserstoff Congress 2008, Schriften des Forschungszentrums Jülich, Volume 12, ISBN 978-3-89336-533-3, Essen, 20.–21 February 2008.

The long-term storage of carbon dioxide produced in power plant processes (carbon capture and storage; CCS) can help to significantly reduce CO_2 emissions. The technique of coal gasification is also an option, which involves first converting coal into a feed gas (H_2 and CO; integrated gasification combined cycle (IGCC)).
Four demonstration plants put into operation between 1994 and 1997 showed no economic or environmental advantages. In 2005, the situation changed completely with the introduction of the emission trading system.
On the one hand, for original IGCC characteristics (high pressure, low volume fluxes, high relevant gas concentrations after CO shift), CO_2 separation can be performed under the best conceivable conditions, and on the other hand, hydrogen can (optionally) be produced as a zero-CO_2 coal product if conversion into electricity is

(partially) done without. These advantages gave rise to new coal gasification projects worldwide.
In addition to the use of conventional physical CO_2 scrubbing, the application of H_2 membranes is also an option, where concentrated "pure CO_2" is captured on the retentate side. This side has already been pressurized and can be immediately further compressed and thus liquefied. The hydrogen, in contrast, loses pressure during permeation and must be recompressed (with additional energy) unless suitable pressurized sweep gases are present in IGCC and can be directly fed into the permeate side of the membrane (or conditioned for this).
This paper describes preliminary process engineering analyses performed at IEF-3 in Forschungszentrum Jülich, as well as work performed at IEF-1 focusing on developing graded porous membrane structures for H_2/CO_2 separation. Parallel to this, work also concentrated on using membranes for CO_2/N_2 separation in flue gases (test planned under real power plant conditions). Challenges include realizing stable mechanical transition structures of macroporous substrates on ultimately nanoporous TiO_2-ZrO_2 functional layers using appropriate interlayers, as well as the achievement of high H_2 and CO_2 permeabilities (non-isolated pores in the nanostructures, no pore blockages caused by steam molecules, very thin top layer) for simultaneously sufficient selectivity of H_2 from CO_2 and CO_2 from N_2. The required homogeneous nanopores are formed from limited distributions of particle and nanoparticle sizes. These were formed in turn by "nanostructure construction kit tools":
variable fabrication routes (incl. sol gel) and variable TiO_2-ZrO_2 mixing ratios.

Nazarko, J.; Zhao, L.; Riensche, E.; Blum, L.

Stoffliche und energetische Analyse der CO_2-Abtrennung aus dem Rauchgas eines Kohlekraftwerkes mit CO_2/N_2-selektiven Membranen
(Mass flow and energy-based analysis of CO_2 separation from the flue gas of a power plant with CO_2-N_2 selective membranes)

Emissionsminderung 2008, VDI-Tagung, Nürnberg, 9-10 April 2008, VDI-Berichte 2035, 233-236.

There are three different power plant concepts that can be used to separate the greenhouse gas CO_2. These are based on the following gas separation processes:
Post-combustion capture (CO_2 separation in the flue gas using CO_2/N_2 separation)
Oxyfuel processes (CO_2 enrichment in the flue gas by means of combustion in oxygen atmosphere generated by air separation using O_2/N_2 separation), and pre-combustion capture (CO_2 enrichment in the synthesis gas with subsequent H_2/CO_2 separation).
In principle, gas separation can be performed in all three cases using membranes. At Forschungszentrum Jülich, researchers are developing suitable inorganic porous and dense (ionic or protonic-electronic mixed conductor) membranes. Parallel to this, future power plant concepts with a focus on post-combustion and oxyfuel are being developed and analyzed. The concepts being pursued differ according to the operating conditions of the membrane and the corresponding technical membrane environment (pressure level on the feed gas and permeate sides, membrane temperature, multi-stage membranes, and others). As the literature does not contain any detailed analyses on CO_2 separation from the flue gas of a coal power plant using membranes, research in this area is essential.

Zhao, L.; Riensche, E.; Menzer, R.; Blum, L.; Stolten, D.

A parametric study of CO_2/N_2 gas separation membrane processes for post-combustion capture

Journal of Membrane Science 325, 284-294 (2008).

Capture of CO_2 from flue gases produced by the combustion of fossil fuels and biomass in air is referred to as post-combustion capture. Chemisorbent processes are considered to be the most feasible method and are already at an advanced stage of development, but gas separation membranes are attracting more and more attention as a possible alternative. This paper describes a detailed parametric study of mass and energy balances for a simulated single membrane process. Typical operating conditions (CO_2 concentration in the flue gas, pressure and temperature, etc.) together with the influence of the membrane quality (permeability, selectivity) and membrane area on membrane performance (CO_2 separation degree and CO_2 purity) are simulated over a wide range of parameters.

Important patents

Patent applications:

Principal inventor	PT	Description
Dr. E. Riensche	1.2327	Device and method for CO_2 separation from a process gas
Dr. E. Riensche	1.2328	Device and method for CO_2 separation from a process gas
J. Nazarko	1.2341	Device and method for reducing CO_2 emissions in the flue gases of combustion plants
Dr. E. Riensche	1.2366	Membrane power plant and technique for operating the same
R. Menzer	1.2381	IGCC power plant with flue gas recycling and sweep gas
J. Nazarko	1.2382	Combustion plant and technique for operating the same
Dr. E. Riensche	1.2405	IGCC power plant with flue gas recycling and sweep gas

Patents granted:

Principal inventor	PT	Description
Dr. E. Riensche	1.2122	Process for generating electricity and heat

5

Outlook

Outlook for future R&D projects

- Future R&D activities at IEF-3 within the framework of the second phase of HGF program-oriented funding

5.1 Future R&D activities at IEF-3 within the framework of the second phase of HGF program-oriented funding

Challenges and objectives

In energy research, one of the biggest scientific challenges today is to combat imminent bottle necks in the energy supply sector. Fast population growth and rapid industrialization in emerging countries such as India and China will see the global energy demand rise drastically in the future and seriously impact on our fragile environmental and climate system. Furthermore, primary fossil energy carriers are becoming increasingly scarce, which will see Germany and Europe becoming even more dependent on imports from countries that are rich with resources.

The primary objective of energy research must therefore be to use new strategies and technologies in order to guarantee a largely independent energy supply system that is both ecologically and economically sustainable and can meet the needs of future generations. In addition, energy technology goods have become important and successful exports which strengthen the competitiveness of German industry and help to maintain and consolidate jobs.

The strategy of the Helmholtz Association of German Research Centres (HGF) details the objectives for the area of energy as the development of long-term alternative, high-performance and permanently exploitable energy sources and conversion techniques, which will be capable of replacing energy carriers with a limited time horizon. At the same time, innovative technologies for the efficient and effective conversion, storage and utilization of primary and alternative energy forms are to be developed. This will allow the global energy demand to be drastically reduced and will give rise to an accompanying, significantly improved yield from resources. Researchers in the HGF centers involved in the "Efficient Energy Conversion and Use (REUN)" program are working on this issue. The key points in the REUN program for the period 2010 – 2014 (the second phase of program-oriented HGF funding) have been defined by the centers active in the program and will be reviewed by a committee composed of well-respected international members.

Program structure and participating centers

Forschungszentrum Jülich, Forschungszentrum Karlsruhe and the DLR are involved in the "Efficient Energy Conversion and Use" program. The program budget in terms of full costs is approx. € 47 million, whereby approx. 45 % of this sum has been allocated to Forschungszentrum Jülich, while Forschungszentrum Karlsruhe receives approx. 31 % and DLR approx. 24 % of the budget. The program is divided into five topics: "Fuel treatment and gas purification", "Power plants", "Fuel cells", "Superconductors", and "Energy-efficient processes". This structure provides a comprehensive description of the process chain from the generation of energy using primary, alternative and substitute fuels right up to energy applications for all of the energy flows produced during these processes. An overview of the person-years invested by the three centers in the different subfields is shown in Tab. 5.

Based on the primary energy mix today and the scenarios of the future, the proportion of renewable energy carriers must be increased and the efficient use of fossil primary energy carriers and solid waste material consolidated. Activities within the framework of the REUN program therefore concentrate on increasing the utilization of existing power plant systems,

fuel cells and other energy conversion processes, as well as on the development of new efficient zero-emission power plant designs which allow the use of biofuels and alternative coal-based fuels. Jülich contributions to the topic of fuel cells will be presented in the following sections.

Program/Topic	DLR	FZJ	FZK
Efficient energy conversion and use	**90 PY**	**172 PY**	**118 PY**
Fuel treatment and gas purification	-	-	42 PY
Power plants	58 PY	52 PY	16 PY
Fuel cells	25 PY	120 PY	-
Superconductors	-	-	25 PY
Energy efficient processes	7 PY	-	35 PY

Tab. 5: Person years invested per center and topic in the REUN program (basic funding only)

Fuel cells

Fuel cells convert chemical energy directly into electricity with an unusually high efficiency and they outdo conventional applications both in terms of stationary local power generation and in the transport sector for drives and on-board power supply. Furthermore, with regard to local emissions, power generation using fuel cells is inherently more environmentally friendly. Due to a higher efficiency and the fact that it uses other fuels, it also boasts a significant reduction in CO_2 emissions. Since fuel cells ultimately rely on hydrogen in the chemical conversion chain, they represent a decisive element on the way towards a low-carbon future.

HGF research activities are based on the solid oxide, direct methanol, and high-temperature polymer fuel cells as well as on reformers. Applications aim towards local power plants as well as on-board power generation for traction in small vehicles and for supplying ancillary components. Cells, stacks and systems are being developed in this program for the areas of application listed above. Objectives include improving lifetime, improving suitability for dynamic operation and general robustness, as well as reducing costs. Fabrication techniques and quality management tools are also being developed in addition to analytical tools for lifetime predictions and particularly for explaining structure-activity relationships.

5.1.1 Direct methanol fuel cells (DMFCs) for light traction

The aim of this work is to develop DMFC energy systems for light traction, for example in the field of material handling, which can replace existing lead batteries both with respect to structure and energy. The necessary requirements for this substitution are:

- the DMFC system must be operated in a water-autonomous manner with an overall efficiency of more than 25 % at ambient temperatures of up to 35 °C,

- during a period of operation lasting at least 5,000 h, the degradation in performance must be less than 25 %,
- the total costs of the DMFC system must be reduced further.

Work will focus on increasing the overall efficiency and the power density of the fuel cell system, identifying and preventing degradation mechanisms in the stack, reducing material and production costs for MEA and stack components, while at the same time increasing quality and reproducibility. Highly integrated plant engineering, the optimum integration of the fuel cell into energy systems, and the realization of water-autonomous system operation will also be investigated. Important supporting activities include the modeling of relevant transport processes in the sensitive components of the MEA and the stack, analysis as part of studies on the structure-activity relationship of functional layers, and the spatially resolved electrochemical and physicochemical characterization of fuel cell components.

5.1.1.1 MEA development

The application of new materials (catalyst, membrane, diffusion layer) and the further optimization of the media and current distribution in the electrodes are intended to reduce the water and methanol permeation from the anode to the cathode side and to improve cell performance. Planned research in the fields of analysis, modeling and simulation will establish a more profound, fundamental understanding of the physicochemical processes. This understanding is urgently needed in order to reduce the noble metal loading required while simultaneously increasing the performance of MEAs. It is also essential for understanding degradation effects in fuel cell components. The results obtained will be directly applied to develop the respective components further. According to the present level of knowledge, the properties of fuel cell electrodes are different in stationary mode than in dynamic operation. With respect to long-term stability, more attention will therefore be focused on electrochemical reactions in single cells and stacks in dynamic operation.

5.1.1.2 Analysis

Physicochemical analysis techniques are used to address the issue of structure-activity relationships in a DMFC-MEA. One of the decisive aspects for imaging the microstructure of DMFC components right down to the nanometer scale is the artifact-free sample preparation of fragile, wet polymers. The objective is to gain a deeper fundamental understanding of the physicochemical processes in fuel cell components and to use this understanding to develop measures that will increase their performance and reduce degradation phenomena. The following methods will be used for this:

- Scanning electron microscopy studies of the morphology and element distribution inside membranes, catalyst layers and MEAs provide important information for identifying the prevailing degradation mechanisms.
- Reproducible fabrication of MEA cross-sections using the ion-beam preparation technique.
- Spatially resolved measurements of current density distribution using magnetic tomography and measurements using segmented cells make will enable the weak points of the components to be determined under operating conditions.

- Experiments on aged stack MEAs using spatially resolved mass spectrometry and nano-XPS will allow us to draw conclusions on local degradation effects during system operation.
- Physical properties must be determined using porosimetry, mechanical and rheological tests, and weathering experiments in order to ensure that potential materials fulfill their application profiles, and to identify ways of increasing the performance of materials already in use.

5.1.1.3 Manufacturing techniques

New automated manufacturing techniques for MEA components will make an important contribution to quality, reproducibility and the reduction of material and production costs. The fabrication process will be adjusted appropriately depending on the characteristics of the materials used. Further improvements in the reliability and lifetime of fuel cells will be achieved by developing automated fabrication and assembly techniques for cell and stack components in combination with suitable process controls.

5.1.1.4 Stack-development

Work will concentrate on investigating the flow configuration in the stack (two-phase flow with small excesses of the reactants) and on possible interactions between the cells. With respect to fabrication, attention will focus on developing inexpensive production methods further. The aim is to ensure homogeneous pressure distribution in the cell and a good dimensional compliance of the flow distribution structures with low production costs.

5.1.1.5 Systems development and verification

Experiments on condensation with inert gas in combination with modeling will lead to the development of highly efficient, compact water recycling systems, which are indispensable for water-autonomous operation. Emissions from the fuel cell system will be reduced to a minimum by identifying suitable operating parameters and, if necessary, by developing compact exhaust-gas cleaning systems. The design and practical testing of functional models close to market maturity are the objectives of a joint development project being pursued in cooperation with an industrial consortium.

5.1.2 High-temperature polymer electrolyte fuel cells (> 160 °C) for on-board power supply

Forschungszentrum Jülich will develop a HT-PEFC stack technology with a power ranging from 5 to 50 kW_{el} within the next five years and prepare this technology for field tests. In order to realize this objective, the graphitic HT-PEFC stacks developed at Forschungszentrum Jülich with the aid of modeling and simulation will be refined. Commercial membrane electrode assemblies (MEAs) and MEAs developed at Jülich will be used in these stacks. In addition to electrochemical studies, analysis and modeling will play an important role in achieving the planned objectives.

5.1.2.1 MEA development

The main components in cells and stacks are MEAs, which are commercially available from BASF, for example. MEA development at Forschungszentrum Jülich shows that it is possible to develop cost-effective alternatives with comparable performance behavior. ABPBI membranes (poly-2,5-benzimidazole) from one supplier are used as the starting material. The membrane is doped with phosphoric acid when the MEA is being assembled using the gas diffusion electrodes developed at Forschungszentrum Jülich. MEAs are currently fabricated on a laboratory scale. Development aims are:

- The further development of coating technology beyond the laboratory scale: at the end of the planned five-year period, MEAs will be fabricated in automated coating and assembly processes. At this stage, we should be able to transfer the technology directly to industrial companies.
- An increase in power density: the focus will be on reducing cathode losses caused by phosphate adsorption at the catalysts.
- An increase in lifetime: studies will concentrate on carbon corrosion under cyclic operating conditions. Changes in the catalyst structures caused by agglomeration and migration will also be investigated. Structural changes will be analyzed in the Jülich fuel cell analysis laboratory.

5.1.2.2 Stack development

The aims of stack development are:

- The development of oil-cooled stacks in the power range of 5 – 25 kW_{el} and air-cooled stacks up to 5 kW_{el} with high gravimetric and volumetric power density.
- An increase in lifetime by expanding our basic understanding of the degradation process that occur and then applying this knowledge in technologies that improve lifetime and facilitate the parallel development of suitable system management strategies.
- A reduction in the cost of stacks by optimizing materials and developing automated fabrication techniques for components and stacks.

5.1.2.3 Analysis

The use of analysis techniques to characterize HT-PEFCs allows us, for example, to determine the leaching of phosphoric acid during cell operation in MEAs developed at Forschungszentrum Jülich. The catalyst degradation effects and carbon corrosion phenomena caused by potential are even more dominant factors. The analyses will be used to explain structure-activity relationships inside the MEAs. The aim is to increase stability and performance by revealing the main (degradation) mechanisms on the meso-, micro- and nanoscales. Moreover, the development of catalyst dispersions will be supported. The following methods will be used:

- Spatially resolved chemical and electrochemical characterization to determine weak points in MEAs, cells and stacks in operation.
- Mechanical strength studies on MEAs.

- Analysis of the morphology and element distribution in membranes, catalyst layers and MEAs using electron microscopy.
- Reproducible fabrication of MEA cross-sections using ion beam preparation as preparatory work for Structural analysis of catalyst dispersions for the production of reproducible processable dispersions for the fabrication of more powerful MEAs.SEM studies.
- Structural analysis of catalyst dispersions for the production of reproducible processable dispersions for the fabrication of more powerful MEAs.
- Structural elucidation of catalytically active centers and their degradation by combining optical spectroscopy with nm resolution and spatially resolved mass and electron spectrometry on the nanoscale.

5.1.2.4 Modeling and simulation

Modeling and simulation are indispensible tools for the efficient development of cells and stacks. At Forschungszentrum Jülich, HT-PEFCs are modeled and simulated on a stack, cell and cell component level. Cells and stacks are designed and fabricated with the aid of scientifically based simulation methods. This work supports and accelerates hardware development.

Moreover, both the underlying models and mathematical methods will be further developed in order to provide answers to the basic questions within fuel cell research. Modeling and simulation therefore play a key role in clarifying structure-activity relationships, as has been demonstrated by research in cooperation with the Institute for Stochastics at Ulm University. The fine structure of gas diffusion layers analyzed by means of imaging techniques was described as a model using stochastic methods. In order to verify that the models and the measured 3D data were equivalent, spherical contact distribution functions were compared. The porosities and tortuosities, calculated from the stochastic fine structure models can then be integrated into material transport simulations as integral structural parameters. This allows changes in the GDL fiber fine structure to be illustrated with respect to material transport. Conversely, requirements in terms of the desired GDL structure can be derived from the specified material transport behavior. The aims of HT-PEFC modeling and simulation are:

- The development of a CFD model (“integrated volume”) describing multicell HT-PEFC stacks with the aim of predicting the operating performance of a projected stack. The model will be verified using current-voltage measurements as well as local current density and temperature measurements. This work will be conducted in cooperation with NRC, Canada. We will add our own user-defined functions to the open-source CFD tool “OpenFoam” and port it onto the supercomputers at Forschungszentrum Jülich.
- The further development of existing detailed high-resolution CFD cell models. These models will be used to design the channel and connector structures of flow distributors. In addition to mapping the electrochemistry, we will also consider the interaction between channel-connector structures and the gas diffusion layer.
- The direct coupling of stochastic GDL fine structure models with numerical simulations. A number of implementations of the fine structure (equivalent in terms of stochastics) will form the basis for numerical simulations. The statistical evaluation of simulation runs will generate parameterized results, which will then be applied in CFD

cell models. This work will be conducted in cooperation with mathematical institutes at the University of Ulm.

- The analytical one-dimensional model of a high-temperature PEFC developed in cooperation with Moscow State University will be refined. This model will illustrate the influence of degradation effects on the operating performance, particularly on structural changes inside the MEA. Structural changes in MEAs will be determined by applying experimental analytical methods. The model will be verified by electrochemical cell measurements and measurements of current density distribution.

5.1.3 Fuel processing systems for the production of H_2 from middle distillates for fuel cells

Using fuel processing systems (autothermal reforming, water-gas shift reaction, catalytic combustion), it is possible to produce hydrogen from readily available energy sources such as liquid petroleum gas (LPG), gasoline, diesel, kerosene and fuel oil, which can be used in local, transportable, portable and mobile applications. When the product gas of the reforming process, known as reformate, is used directly in a fuel cell, the hydrogen contained within it is referred to as “short-lived hydrogen”. In the long term, some of the liquid energy carriers required today could be produced from biomass. In this respect, future research work should focus on second-generation biofuels, which enable the whole plant to be used.

At Forschungszentrum Jülich, research concentrates on short-lived hydrogen produced from middle distillates (kerosene, diesel, and fuel oil) and synthetic fuels similar to middle distillates, such as Fischer-Tropsch diesel and Fischer-Tropsch kerosene from biomass. The proportion of middle distillates in the fuel consumed will continue to increase in the future. The use of middle distillates in fuel cell systems will open up the greatest possible range of applicaitons. The goal of work at Forschungszentrum Jülich in the field of fuel processing is to provide fuel cell systems within the next five years that work on diesel, kerosene and fuel oil and provide an electric power of 15 – 50 kW. Fuel processing units will have a robust long-term stability of 5,000 hours. R&D work on fuel processing can be broken down into three main areas.

5.1.3.1 Desulfurization

Fuels such as kerosene and fuel oil must be desulfurized to a level of less than 10 ppm in order to avoid catalyst poisoning in the reformer. We plan to implement the very promising process paths on an industrial scale. In contrast to industrial refinery processes, the catalytic reaction between the sulfur-containing components and hydrogen (hydrofining) will be combined with hydrogen presaturation in the liquid phase. Hydrofining can be performed on board or at the airport. Pervaporation membranes represent an alternative for preliminary cleaning and adsorbers for deep desulfurization. Suitable materials will be developed and tested in cooperation with universities. The reaction conditions must be optimized for the regeneration of adsorption materials. The materials used, their desorption performance, and the available active adsorption sites must be analyzed with the aid of BET, TPD, TPO and TPR studies.

5.1.3.2 Reforming

In reformate production, the autothermal reformer is the core component. Fuel is fully vaporized here, mixed with atmospheric oxygen and water vapor and then catalytically converted into a hydrogen-rich gas. No side reactions should occur as these could lead to carbon-containing deposits on parts of the reformer and catalyst. Furthermore, complete conversion must be guaranteed. In order to achieve this objective, supercomputers are used to perform advanced calculations of the educt flows and the dimensions of the vaporizer and mixing chamber. A high-speed camera is used to make the fuel spray visible and to provide experimental verification. Previous results must be transferred to the 15 – 50 kW_{el} scale. The possibility of reforming other fuels, such as biomass to liquid (BTL), kerosene and fuel oil, has yet to be explored, as does the question of whether bunker gas oils can be added.

5.1.3.3 Systems development and verification

The fuel processing unit consisting of an autothermal reformer, a water-gas-shift reactor, a catalytic burner, and possibly a CO purification unit and a desulfurization step, can be combined with the SOFC, HT-PEFC and PEFC fuel cell types. At Forschungszentrum Jülich, a priority is the combination with the HT-PEFC. Work on CO fine cleaning for PEFCs will be conducted within the framework of cooperation projects. Research topics include heat recovery in the system (pinch-point method) and start-up behavior. The system can be used in the 15 – 50 kW_{el} power range for on-board power supply in heavy goods vehicles, ships, rail vehicles and aircraft.

5.1.3.4 Process and system analysis

If highly efficient fuel cell systems are to be successfully developed for the market, then trends in the development of the energy supply mix in the energy use sectors and the development of competitive technologies must be taken into consideration. In this regard, relevant well-founded estimates related to energy carriers are systematically based on describing the stages in complete process chains with their respective characteristic conversion losses and environmental impacts. Activities at Forschungszentrum Jülich are devoted to a detailed analysis of the process steps that have not yet been adequately described. In particular, this concerns the provision of second-generation biogenic fuels with respect to their potential and also to their risks in terms of volume as well as the conversion efficiency that can be achieved during production.

In addition, biogenic fuels might have a different impurity profile than fossil fuels and therefore have a different influence on degradation, particularly in DMFCs and most probably also in HT-PEFCs. One of the milestones for the period from 2010 to 2014 is the creation of a comprehensive evaluation basis for biofuels, which on the raw materials side compete with alternative forms of bioenergy use and with food production. Particular attention will be given to the production of biomass-based synthetic fuels that are suitable for APU applications in the various transport sectors.

With respect to the use of fuel cell systems in mobile, stationary, and portable applications, another priority in terms of analysis work is comparing these systems with competing technologies. Milestones here for the period from 2010 to 2014 are the evaluation of the prospects of mobile fuel cells in comparison with advanced internal combustion engines and hybrid drives, as well as with electric drives based on sophisticated battery technologies.

5.1.4 Planar cells with thin functional layers for reduced operating temperatures and longer lifetimes

This topic will focus on basic materials development and the fabrication of components up to the cell level. This includes modeling, degradation analysis and accelerated testing on this level with a focus on fundamental and material-related aspects. A firm basis in cell and stack materials was created in the first POF period (using basic funding and third-party funding). The next period will be dedicated to reducing layer thickness in order to decrease cell resistance (area-specific resistance (ASR)) and to reduce costs. Furthermore, a reduced resistance will allow operation at lower temperatures. This approach should be preferred to higher power.

5.1.4.1 Material and cell development

Forschungszentrum Jülich is equipped with different processing facilities, which can be used to apply optimized layers and coatings. If high-quality coatings are to be produced, modified and adapted substrates are essential. Recent processing work has focused on the evaluation of PVD, sol-gel, roll coating and LPPS-TF techniques for applying thin layers. Rapid thermal processing (RTP) is used to a certain extent to thermally treat deposited structures. Planned future activities comprise:

- adapting materials and material processing for thin-film deposition,
- optimizing layer deposition, and
- characterizing the components produced, including cell, stack and system tests.

The layers applied include all functional and protective layers constituting a cell and the insulating, protective and contact layers inside a stack.

It is important that the technologies used in the research context are compatible with the mass production technologies used in industry. This is the reason why tape casting and screen printing will constitute the backbone of future cell production. Parallel to this, new approaches to stack design, which are suitable for mass production and involve less material, will be devised in order to achieve improved mechanical and thermodynamic characteristics and to significantly reduce costs.

Operation at temperatures as low as 600 °C is currently being tested within the framework of the EU project SOFC600. This is the lowest limit that is assumed for internal reforming operations in SOFC stacks. For applications that use reformate (i.e. from diesel), the temperature could be reduced further. This will open up new opportunities for reducing the degradation caused by corrosion processes. Materials development will therefore aim to achieve an operating temperature of 400 °C. Compared to HT-PEFC technologies (maximum low % CO allowed), this leads to improved CO tolerance while retaining the ability of the SOFC to process CO as a fuel. On the other hand, all requirements associated with start-up time, heat losses, thermal cycling stress, etc. are drastically reduced and the danger of re-oxidation avoided. Operating an SOFC at 400 °C constitutes a high risk and a challenge that is appropriate for a Helmholtz center.

5.1.4.2 Modeling and simulation

Modeling and simulation will accompany the development process on all relevant levels. Research will concentrate on the numeric modeling of fuel cells and fuel cell components.

The aim is to improve our understanding of the underlying physics and chemical reactions and to identify optimum operating conditions and novel designs for cells and cell components. Detailed material, layer and cell models (multilayer systems) are too complex to be used when simulating SOFC stacks or systems. As a result, a special method has been developed in Jülich to couple models at various different levels. This will be described in the relevant sections on stacks and systems.

5.1.4.3 Degradation analysis

Degradation is one of the major issues currently being targeted in fuel cell research. A variety of chemical, mechanical, and physical mechanisms lead to deterioration in fuel cell performance. Within the framework of the integrated EU project “Real-SOFC”, coordinated by Forschungszentrum Jülich, basic research was performed on analyzing and reducing degradation in SOFCs. Jülich will continue to conduct fundamental research aiming to identify the causes of degradation. Specially designed experiments will allow the experimental conditions to be accurately controlled, thus making it possible to study the influence of individual parameters, such as temperature, oxygen partial pressure, overpotential, current flow and fuel utilization. Models of degradation phenomena will be developed and tested for their predictive qualities using the extensive experimental and analysis laboratory facilities, quantitative image analysis and modeling.

The use of analytical techniques is a key element in Jülich fuel cell research and development. Work in the area of physicochemical analysis is concerned with the structure of functional layers and the spatially resolved characterization of fuel cell components. The SOFC group therefore works very closely together with the Central Division of Analytical Chemistry (ZCH) at Forschungszentrum Jülich. Here, the development of adequate analysis methods plays an important role. Applied methods include:

- microscopy and chemical analyses
- high-resolution mass spectrometry (FTICR-MS) of the gas phase after online microsampling from the SOFC during operation, particularly with contaminated fuels (e.g. biofuels)

The aim is to obtain an in-depth basic understanding of the physicochemical processes in fuel cell components and to use this understanding to develop measures that will increase their performance and reduce degradation phenomena.

- The combination of bulk chemical analytical techniques (ICP-OES, ICP-MS) with high local resolution techniques in both elemental characterizations (LA-ICP-MS, SIMS) with organic analysis tools from the mm range to the µm range (µ-Raman) reveals the transport influences in degradation processes.
- Scanning electron microscopy studies of the morphology and element distribution inside membranes, catalyst layers and cells will provide important information for identifying the prevailing degradation mechanisms.
- Experiments on cells removed from stacks after operation (pre-aged cells) using spatially resolved mass spectroscopy and nano-XPS will allow conclusions to be drawn on local degradation effects during system operation.
- Tip-enhanced Raman spectroscopy (TERS), spatially resolved IR and MALDI-MS will be applied to determine the structure of single “dead” reaction centers on a

nanometer scale, particularly in combination with spatially high-resolution MS and nano-XPS for cells that are used with both pure and contaminated fuels (various methane qualities).

Whilst analysis tools are being further implemented and refined, new approaches are just as necessary. One of these is the integration of degradation processes into highly detailed modeling (layers and CFD) in order to implement the mechanisms identified experimentally in a theoretical representation. The models will also serve to predict experimental behavior and to qualify and validate hypotheses. Similarly, the development of new diagnostic methods is necessary to assist the evaluation of degradation and failure modes, by supplying online real-time insights without biasing or destroying experimental data.

Similar approaches and methods will lead to quality assurance procedures during industrial manufacturing. Much fundamental work is still necessary in developing quality monitoring techniques to scan and assess SOFC components in continuous production processes. The methods range from radiometry, IR and ultrasonic scanning to simple mechanical tests and integrity checks. In all cases, a detailed understanding is necessary of failure modes, the correlation between microstructures and macrodamage, as well as acceptable and reject quality characteristics. A solid basis in basic research is indispensable for this.

5.1.4.4 Accelerated testing

Due to the prolonged stack lifetimes recently achieved with Jülich technologies (low degradation), it has become extremely important to accelerate the degradation processes in SOFCs in order to achieve evaluation times that can still be handled in laboratories. The problem is finding methods to increase degradation rates without altering the underlying processes. Accelerated lifetime testing will therefore be one of the priorities of analysis and methodology development at Jülich. Within the scope of the topic of fundamental layer and cell development, work will concentrate on designing special experiments to control acceleration of degradation in single layers and interfaces. Forschungszentrum Jülich will establish an infrastructure of specialized test rigs which will be used to investigate the degradation phenomena in detail and perform accelerated testing. Using the models described above, effects can then be aggregated and calibrated at a later stage using results from accelerated degradation as described in the section on stacks.

5.1.5 kW-class stack technology with improved performance, reliability and methods of manufacturing

This topic concentrates on the properties of stacks up to a magnitude of around 2 kW_{el}. The limitation of the stack size is based on an optimized management of financial resources. Depending on the requirements of the program, this does not exclude the regular use of short stacks and the occasional use of the 5 – 10 kW_{el} class of stacks. Work spans the field from stack design, manufacturing and (automated) manufacturing processes and joining technology to electrochemical and thermomechanical modeling and stack degradation mechanisms to lifetime evaluations with accelerated methods.

5.1.5.1 Manufacture and assembly

Solutions for the production of commercial stacks for stationary and mobile applications (in auxiliary power units (APUs)) are becoming increasingly apparent. The results of a project involving DLR, Forschungszentrum Jülich and BMW as an industrial partner are encouraging and show that SOFCs can be implemented in engineering products. Nevertheless, performance is still limited and is not yet fully in line with the expectations of today's consumers. In order to improve the robustness of stacks, new concepts are necessary. We have termed these concepts the "third generation".

Although great progress has been made in the quality assurance of Jülich stacks (compare for example, the results in the Real-SOFC project, where four partners worked with stacks from Jülich), the assessment of increased performance of materials and components requires a statistically sound basis and high reproducibility of the repeating units and stacks. As a consequence, manufacture and assembly of SOFC stacks has to be at least partly automated in order to gain a rigorous control of tolerances. An application was filed in 2008 for HGF investment funds, following a recommendation from the 2007 HGF interim evaluation committee.

The joining of stacks with glass sealant is one of the strategies that has been pursued by Forschungszentrum Jülich for a number of years. The clear advantages associated with this process compared to metallic braze sealing led to this process being gradually adapted by industry. To date, not all requirements have been met in equal measure (for example, CTE, crystallization rate, viscosity, interaction with the metallic oxide layer). The multicomponent system of the glass-ceramic sealant has a number of coexisting phases with different mechanical properties. The process of joining is therefore extremely complex and further work is required to develop glass formulae with a high strength and slow crystallization. This is the key to realizing a reliable stack concept.

5.1.5.2 Design

The designs used at Forschungszentrum Jülich today were mainly devised as laboratory setups to evaluate materials interactions and performance degradation. With the increased interest in stacks for specific applications, Forschungszentrum Jülich has readjusted its focus on designing stacks for stationary and mobile applications capable of functioning under difficult operating conditions (thermal cycles, vibration) whilst minimizing deterioration. At the same time, the manufacturing cost has to meet market demands. Modeling, manufacturing and characterization capacities at Forschungszentrum Jülich will be used to design stacks of the third generation and offer a mid-term perspective for realization at a competitive level. The target size is 1 to 5 kW_{el} per stack module.

5.1.5.3 Degradation analysis

In order to extend the lifetime of stacks, the magnitude and time scale of limiting degradation processes need to be understood. Extensive "real-time" testing of full stacks in dependence on realistic operating conditions, as recently started within the European project Real-SOFC, must be continued. Advanced in situ observations of stack performance during all stages of stack lifetime must also be made possible. These tests must be followed by a full post-test examination of the stack, including detailed (chemical) analyses of the microstructure of components and at interfaces. Due to the complexity of stack operation, tests must also be

developed and performed in parallel on single components and interfaces with a focus on individual degradation processes. Forschungszentrum Jülich will then use its considerable modeling expertise to construct cells and stacks that integrate the degradation aspect, thus leading to lifetime prediction capabilities.

Using the results of these “real-time” tests and our understanding of the magnitude and time scale of the degradation processes at stack level, methods will be developed for accelerated evaluation in order to reduce the time required to determine stack lifetime or to formulate adequate estimates. Once again, this requires extensive testing. More severe unrealistic conditions will be used here to single out and accelerate specific degradation processes.

Another point of interest will be thermomechanics. This field describes the effects of thermal stress on fuel cell components. In order to be able to develop stacks with a full thermal cycling ability (repeated cooling to room temperature), we must first have an in-depth understanding of thermally induced stress and the interaction with mechanical forces (e.g. contacting). This requires the acquisition of basic thermal materials data, the development of the necessary experimental tools required to determine forces in “real” stacks and stack components, the establishment of models (including coupling with electrochemical models), and the development of novel and advanced approaches to obtaining information on mechanical and thermal stress (acoustic, radiometric, optical, etc.).

5.1.5.4 Modeling and simulation

The use of computational fluid dynamics (CFD) as a virtual laboratory has substantially reduced the time and cost associated with designing the geometrical structure of fuel cells compared to physical prototyping when used to evaluate design alternatives. If CFD analyses are implemented during the pre-design phase, manufacturing processes can be optimized in terms of cost and quality. Moreover, CFD provides detailed insights into complex processes and therefore reduces the need for costly experimentation. In addition, CFD is supported by analytical and semi-analytical models on all other scales.

In cooperation with the National Research Council of Canada, a common (SOFC) CFD model is currently being developed on the basis of open-source CFD software OpenFOAM. This model will be made available free of charge for use as a standard by the developers worldwide. It is hoped that the free software will also allow Forschungszentrum Jülich to process large-scale CFD computations on the Jülich supercomputers without having to buy expensive parallel licenses. This will require the programming and implementation of fuel-cell specific routines in the open-source software and the programming of routines required for the parallelization of the software.

5.1.6 Integrated stack module development and systems technology with a rating of > 10 kWel

In addition to the residential and APU power markets (1 to 5 kW_{el}), industrial (commercial) combined heat and power (CHP) units, including polygeneration, are becoming increasingly important for fuel cell applications. These units will have a total rating of 20 to 250 kW_{el}. Since they cannot be built from a multitude of small stacks with sufficient compactness and reliability, ways have to be found to construct large “modules” from several units with a rating of 10 to 100 kW_{el}, which will then be used as building blocks for large systems.

5.1.6.1 BOP components and system verification

Before work begins in this area, it is essential that the limitations for increasing component size (cell size, interconnects, jointing seams, etc.) are understood and that the requirements of cell and the stack for system operation are taken into consideration. Forschungszentrum Jülich will concentrate on the development of concepts and components for such systems. Actual system design and construction will only be targeted in cooperation with industrial partners. The main objectives will be increasing cell size and improving the design of “integrated modules”. This will not only include the SOFC stack (possibly as a multitude of stacks) but also the high-temperature balance of plant components and the ensuing system design. The further development of these hot BOP components with respect to improved function combined with reduced mass and volume also requires detailed modeling and validation by testing.

5.1.6.2 Modeling and simulation

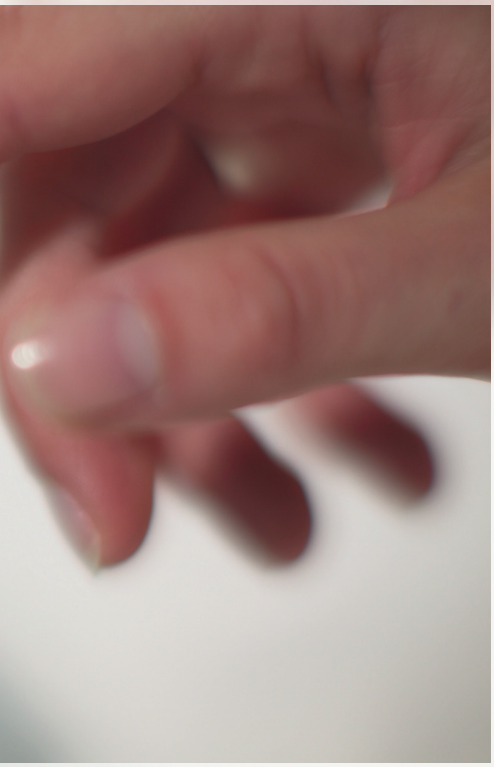
Modeling and simulation are used at all levels of fuel cell development at Jülich. A hierarchy of models has been developed that bridges the field from cell-layer to system. The models vary in complexity corresponding to the level of detail they represent. A special achievement of Forschungszentrum Jülich is the correct depiction of complex processes as a simplified “carry over” from detailed models to aggregated higher-level models, especially for systems. These models will be refined and receive new functionalities in the context of the available supercomputing facilities. The transport of mass, heat, and charge as well as the distribution of chemical and electrochemical reactions, for example, can now be studied on a scale of several micrometers up to a scale of meters. Examples include: the modeling of temperature and concentration profiles in porous substrates (i.e. µm scale) and the distribution of mass, temperature, current, voltage and the rate of (electro)chemical reactions over the volume of a fuel cell stack (cm scale). On the system scale, the behavior of complex fuel cell systems will be studied using the more detailed input from the “lower-level” model. Depending on complexity, the models will be zero to three dimensional, simulating the stationary and/or dynamic behavior of a fuel cell system, respectively.

5.1.7 Expected results and milestones

Using the resources made available by HGF, Jülich fuel cell research and development will conduct basic and application-oriented R&D projects in the six aforementioned fields during the course of the five-year funding period. A topic-based plan foresees activities at Jülich delivering concrete results as shown in Tab. 6. Whether or not these results have been achieved will be assessed every year by the HGF Senate.

Milestones	Date
Automated fabrication of gas diffusion electrodes and catalyst-coated membranes (CCMs) for DMFCs by means of various coating techniques; automated DMFC stack assembly	**2010**
Third-generation SOFC stacks: reliable operation (> 5,000 h) with different fuels (rate of utilization > 60 %) including automated stack fabrication	**2011**
Demonstration of thin-film technology for SOFC cells on an industrial scale: 16-cm² single cells deliver 0.5 W/cm² at 600 °C and a high utilization rate of > 60 % with different fuels	**2012**
Fuel processing of Fischer-Tropsch BTL fuels in an integrated system with a 5-kW_e HT-PEFC	**2012**
Demonstration of a DMFC system for light traction: competitive in terms of cost, performance, and lifetime	**2014**
Design for an integrated submodule for large SOFC systems validated with third-generation stack technology	**2014**

Tab. 6: Expected R&D results and deadlines



6

Data

Facts and Figures

- Institute of Energy Research – Fuel Cells (IEF-3)
- Overview of department expertise
- Publications, technology transfer and resources
- Committe work
- Contributions to trade fairs and exhibitions
- How to reach us
- List of abbreviations

6 Facts and figures

6.1 Institute of Energy Research – Fuel Cells (IEF-3)

The Institute of Energy Research – Fuel Cells (IEF-3) concentrates on the research and development of fuel cells. Work is pursued in four areas: ceramic high-temperature fuel cell (SOFC), direct methanol fuel cells (DMFC), high-temperature polymer electrolyte fuel cell (HT-PEFC), and the reforming and desulfurization of liquid energy carries that could be used to provide hydrogen in fuel cells.

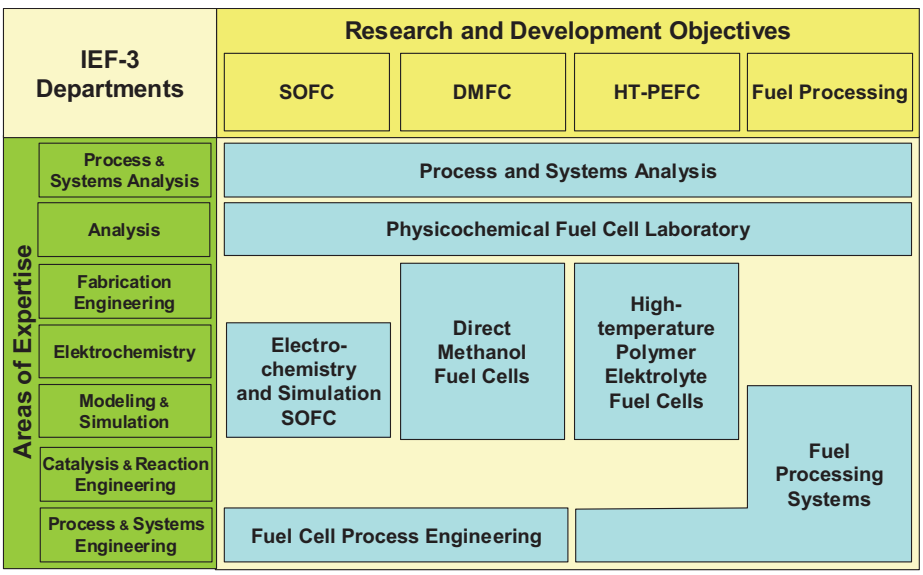
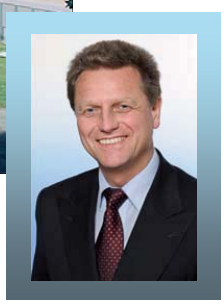


Fig. 135: Departments vs. areas of expertise and R&D objectives of IEF-3

Focusing intensively on a small number of fuel cell types and a restricted power range makes it possible to work on fuel cells with teams of supercritical size beginning with the electrochemical cells and ranging up to process engineering for the whole system. The institute's objectives and focal points are unlocking the synergies between the specialized disciplines and putting theory into practice in order to reach a pilot stage. Stationary, portable and mobile applications up to and including complete systems with fuel cells, together with cost aspects, are evaluated by process and systems analysis in terms of their usability. They are also compared to competing systems from a technical, energetic and economic perspective. Furthermore, application-oriented R&D activities are accompanied by basic research aiming to clarify structure-activity relationships using selected advanced analysis methods.

IEF-3 aims to conduct research work that yields groundbreaking results of social, ecological and economic relevance in comparison with other international research facilities. This quality of work will be achieved by basic research in close coordination with technical development work in relevant scientific and technical fields of expertise. Special significance is attached here to international cooperations with partners from research and industry. The institute concentrates on implementing results from research in innovative products, procedures and processes in cooperation with industry. It is keen to make a contribution to bridging the gap between science and technology. Cooperation with universities, universities

of applied sciences, training departments and training centers is designed to promote opportunities for further education and training.



Prof. Dr.-Ing. Detlef Stolten (Head of IEF-3)
Institute of Energy Research – Fuel Cells - IEF-3
Forschungszentrum Jülich GmbH – D-52425 Jülich
Tel.: +49 2461-61-3076 ; e-Mail: d.stolten@fz-juelich.de

With around 160 employees, Jülich has the largest institutional fuel cell research team in Europe. Of these, around half work on the SOFC, and approx. 1/3 of these are involved in IEF-3 activities. Another two institutes also work in the field of SOFCs: IEF-1 is responsible for manufacturing materials and IEF-2 tests the materials and conducts steel research. The Central Technology Division (ZAT) is responsible for stack construction.

The other 75 or so of the 100 employees at IEF-3 are equally split between low-temperature fuel cells and ceramic high-temperature fuel cells. Each of these two fields has a coordinator for generic topics who also act as initial contact persons. The coordination of activities on the SOFC goes beyond the borders of IEF-3 and involves other participating institutes.

Project Leader
Low-Temperature Fuel Cells
and
Deputy Head of IEF-3

Dr.-Ing. Bernd Emonts
Tel.:+49 2461-61-3525
eMail: b.emonts@fz-juelich.de

Project Leader
High-Temperature Fuel Cells
PBZ

Dr. Robert Steinberger-Wilckens
Tel.: +49 2461-61-2052
eMail: r.steinberger@fz-juelich.de

6.2 Overview of department expertise

Electrochemistry and Simulation SOFC | **Direct Methanol Fuel Cells**

Fields of work, range of services

In Jülich, SOFCs are researched and developed from materials up to entire systems. This department works on electrochemistry and stack tests, as well as modeling from cells to stacks. Cells and stacks are tested under laboratory conditions in order to obtain specific information, and under realistic operating conditions including operation for extended periods of time. In-house models for simulation calculations that take account of the mass, charge and heat transport processes for cells and stacks are applied and refined. The results are used to develop new concepts

Work on direct methanol fuel cells ranges from membrane electrode assemblies to stacks within the department and, in close cooperation with process engineering, up to systems. New materials for membranes and catalysts are characterized, which enables the development and fabrication of innovative membrane electrode assemblies. The structure-activity relationship of the electrode layers is a priority. Stack modeling and design together with new analytical techniques in stack technology, as well as automated fabrication methods on a pilot plant scale, guarantee the bridging function between science and technology.

Facilities, processes, methods

Equipment
- Test rigs for electrochemical investigations of solid oxide fuel cells (SOFCs)
- Test rigs for electrochemical investigations of solid oxide fuel cell stacks
- Apparatus for measuring permeation and diffusion

Models
- Computer models to simulate operating conditions in SOFCs (membrane, cell and stack) on the basis of the transport processes for heat, mass and charge

Equipment
- Test rigs for electrochemical investigations of DMFCs and stacks
- Apparatus for the characterization of membranes for the DMFC
- Desk coater for the continuous fabrication of MEA components
- Robot facilities for automated fabrication of cell components (stamping and hot-pressing) and stacks (assembling)

Contacts

Dr. L.G.J. (Bert) de Haart
Tel.: +49 2461-61-6699
Email: l.g.j.de.haart@fz-juelich.de

Dipl.-Ing. Jürgen Mergel
Tel. +49 2461-61-5996
Email: j.mergel@fz-juelich.de

High-Temperature Polymer Electrolyte Fuel Cells

Fuel Processing

Fields of work, range of services

Work on the HT-PEFC ranges from the electrode to the stack and is conducted in cooperation with internal and external partners. New electrode structures and electrode preparation methods are developed, and MEAs are fabricated and electrochemically characterized. Moreover, intensive studies are conducted on structure-activity relationships in the electrode layers. This work is accompanied by modeling in order to obtain an in-depth understanding of the processes. In addition, simulation activities are pursued on a cell and stack level. This supports the development of air-cooled and liquid-cooled stacks with high volume-specific and weight-related power densities.

Hydrogen for fuel cells produced from commercially available fuels will make it possible to introduce fuel cell technology in a short space of time. The institute specializes in reforming middle distillates – diesel, kerosene and fuel oil. Work is carried out on the entire system, including desulphurization and CO purification. The focus is on reactors in the 3 – 50 kW power class incorporated into high-temperature PEFC or SOFC systems. Complex, realistic models, on which reactor design and construction are directly based, are supported by the use of glass models in which similarity theory is used to image flows.

Facilities, processes, methods

Equipment

- Test rigs for the electrochemical characterization of MEAs
- Test rigs for electrochemical studies on stacks up to 5 kW_{el}
- Equipment for the fabrication of gas diffusion electrodes

Models

- Simulation models to describe mass, charge and heat transport processes in cells and stacks

Equipment

- Test rigs for the investigation of reactors for reforming, water-gas shift reaction, preferential oxidation and desulphurization
- Test rigs for screening and investigating catalysts with regard to activity and selectivity
- Analytical devices to determine concentrations (GC, GC/MS, NDIR) of reaction gases
- Apparatus for fractional distillation of fuels
- CFD simulation program for imaging educt mixture and reactor design

Contacts

PD Dr. rer. nat. Werner Lehnert
Tel.: +49 2461-61-3915
Email: w.lehnert@fz-juelich.de

Prof. Dr.-Ing. Ralf Peters
Tel.: +49 2461-61-4260
Email: ra.peters@fz-juelich.de

Fuel Cell Process Engineering

Physicochemical Fuel Cell Laboratory

Fields of work, range of services

Designing and building efficient fuel cell systems requires detailed knowledge of the cell up to the complete system. The intensive interactions between cells and the system as a whole represent a challenge in terms of development which is fully explored here. Three DMFC test plants (2 kW) and two SOFC test plants (1 kW, 20 kW) were constructed in close collaboration with Cell and Stack Engineering. The focus of the work is on developing new system concepts, testing and evaluating these concepts, developing components in cooperation with industry, and testing and developing control and regulating concepts.

The Physicochemical Fuel Cell Laboratory develops and applies analytical techniques for the in situ and/or spatially resolved analysis of structures and effects. The basic structure-activity relationships of complex processes in fuel cells and reactors are determined and used to improve both. Furthermore, the physical properties of cell components are determined, which serve to verify and establish the mechanical and thermodynamic requirements for their use in fuel cells.

Facilities, processes, methods

Equipment and models

Test rigs for

- high-temperature heat exchangers up to 850 °C and 200 m^3 air/h
- reformers and afterburners for SOFC stacks with a power of 5 kW
- air compressors up to 100 m^3/h and exhaust-gas-heated steam generators for SOFC plants
- process engineering investigations of DMFC stacks and system components
- CFD models to determine flow distribution in stacks
- simulation models for the design of fuel cell plants

Equipment

- Imaging analysis techniques:
  field emission scanning electron microscope (FE-SEM) with integrated energy dispersive X-ray spectroscope (EDX), confocal laser scanning microscope (CLSM)
- Spatially resolved analysis techniques:
  segmented cell technology (SCT), magnetomography, mass spectroscopy (SRMS)
- Physical analysis techniques:
  material testing machine with climate chamber, standard porosimeter with drying chamber, weighing unit and robot, particle size measuring unit (PCCS), environmental test chamber

Contacts

Prof. Ludger Blum
Tel.: +49 2461-61-6709
Email: l.blum@fz-juelich.de

Prof. Dr.-Ing. Detlef Stolten (i.PU)
Tel. +49 261-61-3076
Email: d.stolten@fz-juelich.de

Process and Systems Analysis

Fields of work, range of services

Selecting appropriate energy systems for the future and guiding their development requires a systematic approach, which is used here for fuel cells. The investigations are based on observations of energy chains, benchmarks for other application and manufacturing technologies, and economic comparisons. This broad experimental basis and the more extensive modeling in the institute are used to model entire systems and to compare them with competing technologies under realistic conditions. They are also used to identify development potential and shortcomings. Studies are also carried out for industry and confidentiality of information is assured.

Facilities, processes, methods

Methods

- Design engineering for fuel processing and energy systems with fuel cells
- Integrated evaluation methods (life cycle analyses) for energy systems

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Contacts

Dipl.-Ing. Dipl.-Wirt.-Ing.
Thomas Grube (acting)
Tel. +49 2461-61-5398
Email: th.grube@fz-juelich.de

6.3 Publications, technology transfer and resources

The scientific and technical results of the work carried out at IEF-3 are published in relevant journals and presented to interested specialist audiences at national and international conferences on the subject. Important journals in which peer-reviewed papers from IEF-3 have been published include: Journal of Power Sources (2007: 4; 2008: 1), Electrochimica Acta (2007: 4, 2008: 1), Fuel Cells: From Fundamentals to Systems (2007: 3, 2008: 1), Journal of Fuel Cell Science and Technology (2007: 2, 2008: 1), and Journal of the Electrochemical Society (2007: 1, 2008: 2). The most important conferences in which IEF-3 participated in 2007 were: Fuel Cell Seminar in San Antonio, Texas, USA, with two papers, and the 10th Symposium on Solid Oxide Fuel Cells (SOFC-X) in Nara, Japan, with two papers. In 2008, IEF-3 presented eight papers at the 8th European Solid Oxide Fuel Cell Forum in Lucerne, Switzerland, and eight papers at the 4th International German Hydrogen Energy Congress 2008 in Essen. The various departments within IEF-3 also contributed to numerous other specialist conferences with papers and presentations both within Germany and abroad. In addition, two PhD theses focusing on fuel processing and one focusing on DMFC research and development were completed during the period under review (2007 and 2008). Another PhD thesis was completed and submitted outside IEF-3.

Year		2007	2008
Publcations	Peer-reviewed journals[1)]	26	15
	Books and journals	2	6
	Proceedings	11	40
	PhD theses	2	2
Technology transfer	Ongoing projects with third-party funding	44	45
	Patent applications	16	14
	Patents granted	11	13
Ressources[2)]	Staff (POF[3)]/third-party funds)	89 (66/23)	90 (66/24)
Explanatory Notes	[1)]According to ISI citation index [2)]Data in PY/a [3)]POF: Program orientied funding		

Tab. 7: IEF-3 core data for 2007 and 2008

To ensure successful technology transfer, IEF-3 was involved in numerous R&D projects (2007: 44; 2008: 45) which received funding from the European Commission, the Federal Ministry of Economics (BMWi) and that of Education and Research (BMBF), the corresponding Ministries of North Rhine-Westphalia, and projects financed by industry. IEF-3 was also responsible for managing and coordinating some of these projects. The numerous

patent applications (2007: 16; 2008: 14) and patents granted (2007: 12; 2008: 13) were another step towards smooth technology transfer.

IEF-3 has a staff of just under 100 and is partially financed by program-oriented funding (POF) from the Helmholtz Association of National Research Centres (HGF) and partially by third-party funds. Some of the workforce at IEF-3 is employed on a part-time basis. The effective personnel capacity was 89 PY/a in 2007 and 90 PY/a in 2008.

6.4 Committe work

The expertise of IEF-3 in fuel cells and hydrogen technology, which is renowned both throughout Germany and abroad, is reflected in the fact that several IEF-3 scientists are members of and collaborate with national and international committees. One example of international recognition was the involvement of Professor Stolten in the Global Roundtable on Climate Change (GROCC) and his role as an expert consultant for the current IPCC Report (Intergovernmental Panel on Climate Change). Furthermore, Professor Stolten and Dr. Dohle occupy leading roles on the committees of the International Energy Agency (IEA) responsible for fuel cells. On a national level, Professor Stolten is a member of the advisory council of the National Organization for Hydrogen and Fuel Cell Technology (NOW) where he is the HGF representative for research. The committee work performed by IEF-3 employees on a national and international level is set out in detail below.

Working Group of Electrochemical Research Facilities (AGEF e.V.)
since 2000, Prof. Dr.-Ing. D. Stolten
Member of the Board of Directors

IEA Executive Committee in the "Advanced Fuel Cells" Annex
since 2000, Prof. Dr.-Ing. D. Stolten
Head of the German delegation

Fuel Cell and Hydrogen Network NRW
since 2002, Dr.-Ing. H. Dohle
Head of the Stack Design and Assembly Working Group
since 2006, Dr.-Ing. H. Dohle
Member of the Complete System Working Group

EC Hydrogen and Fuel Cell Technology Platform Advisory Council
since 2004, Prof. Dr.-Ing. D. Stolten
Member

GVC Energy Process Engineering Expert Committee / VDI Society for Process Engineering and Chemical Engineering
since 2003, Prof. Dr.-Ing. D. Stolten
Member of the "Energy Process Engineering" Expert Committee
since 2006, Prof. Dr.-Ing. D. Stolten
Vice Chairman of the "Energy Process Engineering" Expert Committee
since 2008, Prof. Dr.-Ing. D. Stolten
Chairman of the "Energy Process Engineering" Expert Committee

Masterflex AG Supervisory Board
since 2004, Prof. Dr.-Ing. D. Stolten
Vice Chairman of the Supervisory Board

IEA ANNEX XVI: Collaborative Research on Polymer Electrolyte Fuel Cells
since 2004, Dipl.-Ing. J. Mergel
Member

IEA ANNEX XXI: Collaborative Research on Polymer Electrolyte Fuel Cells
since 2004, Dr.-Ing. H. Dohle
Member

Fuel Cell Qualification Initiative
since 2005, Dr.-Ing. B. Emonts
Member of the Executive Committee

BREZEL Expert Committee of the Association of German Engineers
since 2005, Prof. L. Blum
Member of the Expert Committee

Global Roundtable on Climate Change, Columbia University, New York
since 2006, Prof. Dr.-Ing. D. Stolten
Member

Intergovernmental Panel on Climate Change
since 2006, Prof. Dr.-Ing. D. Stolten
Expert for the current IPCC report

DKE "Portable Fuel Cell Systems" Standardization Working Group
since 2006, Dipl.-Ing. J. Mergel
Member of the Working Group

EC Joint Technology Initiative "Fuel Cells and Hydrogen"
since 2006, Dr.-Ing. B. Emonts
Member of the "Research Grouping" core team

National Organization for Hydrogen and Fuel Cell Technology Advisory Board
since 2007, Prof. Dr.-Ing. D. Stolten
Member and HGF representative for research

N.ERGY in EU FCH Undertaking
since 2008, Prof. Dr.-Ing. D. Stolten
Representative of full member Forschungszentrum Jülich

6.5 Contributions to trade fairs and exhibitions

IEF-3 has set itself the objective of showcasing its capacity for innovation by demonstrating new technologies made possible by the institute's R&D priorities. Alongside this, one prominent technology trade fair is selected each year to showcase the proven highlights of the year. At the Hannover Messe in 2007, IEF-3 unveiled the first forklift truck in the world with a DMFC drive (see Fig. 136) to an interested specialist audience. In addition, the core components of a diesel-run on-board power supply with HT-PEFCs were showcased.

Fig. 136: DMFC forklift truck at the Hannover Messe 2007

2007

E-world of energy and water
6.-8.02.2007, Essen, Germany
Desulfurization components

Hydrogen Expo US
19.-21.03.2007, San Antonio, TX, USA
Fuel processing components

Hannover Messe
16.-20.04.2007, Hannover, Germany
DMFC forklift truck, HT-PEFC stack with diesel reformer including shift stages, SOFC system model

Deutsches Technikmuseum Berlin
24.05.-22.07.2007, Berlin, Germany
DMFC components, on-screen presentation, information boards

Forschung und Mittelstand
28.08.2007, Jülich, Germany
Information boards

Highlights der Physik 2007
28.-31.08.2007, Frankfurt am Main, Germany
DMFC folding stack in operation

Korea Energy Show
2.-5.10.2007, Seoul, South Korea
DMFC stack model, information boards

Fuel Cell Seminar 2007
15.-19.10.2007, San Antonio, TX, USA
DMFC forklift truck battery tray, HT-PEFC stack with diesel reformer including shift stages

WissKom 2007
6.-8.11.2007, Jülich, Germany
DMFC forklift truck battery tray and JuMOVe 1 scooter

NRW-Empfang 2007
25.11.2007, Berlin, Germany
DMFC forklift truck

One year later, IEF-3 showcased a more advanced version of the DMFC hybrid system for material handling applications at the Hannover Messe 2008 (see Fig. 137). The modified drive system was subjected to a thorough operational study after it was unveiled at the Messe. The results of this test are outlined in Chapter 3.1. All areas of Jülich fuel cell research were represented at the 30-m² booth as was the case in past years.

Fig. 137: DMFC forklift truck at the Hannover Messe 2008

All of this, plus IEF-3's involvement in ten other trade fairs and exhibitions, saw 2008 as a year characterized by an extensive amount of sales promotions and public relations. The exhibits presented at the different events are listed below.

2008

E-world of energy and water
19.-21.02.2008, Essen, Germany
DMFC forklift truck battery tray

4th German Hydrogen Congress 2008
20.-21.02.2008, Essen, Germany
DMFC folding stack in operation

4th International Hydrogen & Fuel Cell Expo 2008
27.-29.02.2008, Tokyo, Japan
Machine-made gas diffusion electrode (GDE), information board

Hannover Messe
21.-25.04.2008, Hannover, Germany
DMFC forklift truck, HT-PEFC stack with diesel reformer including shift stages, SOFC and DMFC components

SERI 2008
5.-7.06.2008, Paris, France
Information boards, on-screen presentation

17th World Hydrogen Energy Conference 2008
15.-19.06.2008, Brisbane, Australia
Information boards, on-screen presentation

Hamburger Staplertagung
19.06.2008, Hamburg, Germany
DMFC forklift truck battery tray

European Biofuel Congress
24.-25.06.2008, Essen, Germany
DMFC forklift truck, HT-PEFC stack with diesel reformer including shift stages

8th European SOFC Forum
30.06.-4.07.2008, Lucerne, Switzerland
SOFC cell fabrication and stack construction, desulfurization and reforming reactors

4th General Assembly for Hydrogen and Fuel Cell Technology
13.-15.10.2008, Brussels, Belgium
DMFC forklift truck battery tray, HT-PEFC stack with diesel reformer including shift stages, SOFC components

Fuel Cell Seminar 2008
27.-31.10.2008, Phoenix, AR, USA
Machine-made gas diffusion electrode (GDE), information boards, on-screen presentation

6.6 How to reach us

6.6.1 By car

Coming from Cologne on the A 4 motorway (Cologne – Aachen) leave the motorway at the Düren exit, then turn right towards Jülich (B 56). After about 10 km, turn off to the right onto the L 253, and follow the signs for “Forschungszentrum”.

Coming from Aachen on the A 44 motorway (Aachen – Düsseldorf) take the “Jülich-West” exit. At the first roundabout turn left towards Jülich, and at the second roundabout turn right towards Düren (B 56). After about 5 km, turn left onto the L 253 and follow the signs for “Forschungszentrum”.

Coming from Düsseldorf Airport, take the A 52 motorway (towards Düsseldorf/Mönchengladbach) followed by the A 57 (towards Cologne (Köln)) to Neuss-West. Then take the A 46 (towards Jüchen/Grevenbroich), before turning onto the A 44 (towards Aachen). Continue as described in “Coming from Düsseldorf”.

Coming from Düsseldorf on the A 44 motorway (Düsseldorf – Aachen) you have two choices:

1. (Shorter route but more traffic) turn right at the Jülich-Ost exit onto the B 55n, which you should follow for approx. 500 m before turning right towards Jülich. After 200 m, before the radio masts, turn left and continue until you reach the “Merscher Höhe” roundabout. Turn left here, drive past the Solar Campus belonging to the University of Applied Sciences and continue straight along Brunnenstrasse. Cross the Römerstrasse junction, continue straight ahead onto Wiesenstrasse, and then after the roundabout and the caravan dealers, turn left towards “Forschungszentrum” (signposted).

2. (Longer but quicker route) drive until you reach the “Jülich-West” exit. At the first roundabout turn left towards Jülich, and at the second roundabout turn right towards Düren (B 56). After about 5 km, turn left onto the L 253 and follow the signs for “Forschungszentrum”.

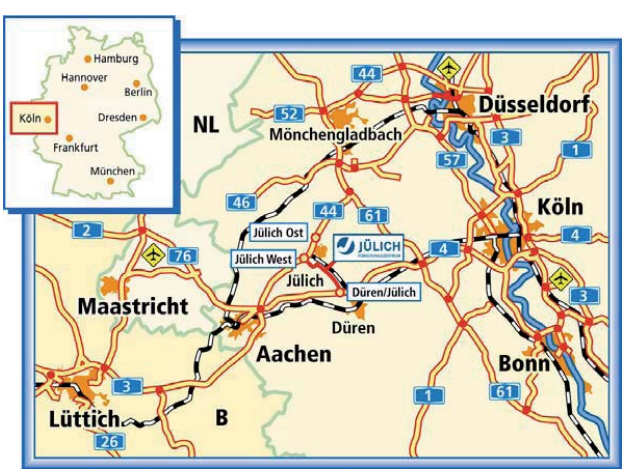

Fig. 138: Euregio Rheinland map

Navigation systems: In your navigation system, enter your destination as “Wilhelm-Johnen-Strasse”. From there, it is only a few hundred meters to the main entrance – simply follow the signs. Forschungszentrum Jülich itself is not part of the network of public roads and is therefore not recognized by navigation systems.

6.6.2 By plane

Cologne Bonn Airport: From the railway station at the airport, take the S13 to Cologne main train station (Hauptbahnhof) and then continue with the regional express to Düren, or go to Köln-Ehrenfeld by regional express and then take the S12 to Düren. Continue from Düren as described in “By train”.

By train from **Düsseldorf Airport**: From the railway station at the airport, travel to Cologne main train station and then continue on to Düren. Some trains go directly to Düren whereas other connections involve a change at Cologne main train station. Continue from Düren as described in “By train”.

6.6.3 By train

Take the train from Aachen or Cologne to Düren’s main train station (Hauptbahnhof). Then take the local train to Jülich (“Rurtalbahn”) and get out at the “Forschungszentrum” stop. From here, you need to keep right and walk towards the main road before turning right towards Forschungszentrum Jülich. The main entrance to Forschungszentrum Jülich is about 20 minutes by foot.

Fig. 139: Forschungszentrum Jülich campus map

Fig. 140: Map showing the Institute of Energy Research – Fuel Cells (IEF-3), Helmholtz Ring H8, building no. 03.2

6.7 List of abbrevations

ABPBI	poly-2,5-benzimidazole
AEL	alkaline electrolyzer
APFO	ammonium perfluorooctanoate
APU	auxiliary power unit
ASC	anode-supported cell
ASR	area specific resistance
ASU	air separation unit
ATR	autothermal reforming
BET	method for determining specific surface area developed by Stephan Brunauer and Emmett and Edward Teller
Bfe	Federal Technology Centre for Electrical Engineering and Information Technology (ger.: Bundestechnologiezentrum für Elektro- und Informationstechnik e.V.)
BiP	bipolar plate
BMBF	German Federal Ministry of Education and Research (ger.: Bundesministerium für Bildung und Forschung)
BMW	bavarian engine factory (ger.: Bayrische Motorenwerke)
BMWi	Federal Ministry of Economics (ger.: Bundesministerium für Wirtschaft)
BOP	balance of plant
BSCF	barium-containing perovskite
BTL	bio-to-liquid
CAD	computer-aided design
CCD	charge-coupled device technology
CCM	catalyst-coated membranes
CCS	carbon capture and storage
CE	Certification Europe (fr.: Conformité Européenne)
CFD	computational fluid dynamics
CGO	cerium gadolinium oxide: $Ce_{0.8}Gd_{0.2}O_{2-\delta}$
CHP	combined heat and power
CONRAD	measuring instrument: Cold Neutron Radiography and Tomography
CTE	coefficient of thermal expansion
CYCLE-TEMPO	program for the modeling of process engineering systems
DC	direct current
DLR	German Aerospace Center (ger.: Deutsches Zentrum für Luft- und Raumfahrt)
DMFC	direct methanol fuel cell
DSC	differential scanning calorimeter
EB-PVD	electron beam physical vapor deposition
EC	European Commission
ED	electronic domain
EDX	energy dispersive X-ray spectroscopy
EEG	law on the priority of renewable energies (ger.: Erneuerbare Energien-Gesetz)
EL	extra light (ger.: Extra Leicht)

ENSA	project for the development of SOFC APUs
EU	European Union
FE-SEM	field emission scanning electron microscope
FhG-ISI	Fraunhofer Institute for Systems and Innovation Research (ger.: Fraunhofer Institut für Systemtechnik und Innovationsforschung)
FKM	fluorocaoutchouc with vinylidene (di)fluoride as a monomer
FMEA	failure mode effect analysis
FTICR-MS	high-resolution mass spectrometry
FTIR	Fourier transform infrared spectroscopy
GD	galvanic domain
GDE	gas diffusion electrodes
GDL	gas diffusion layer
GenFC	generic fuel cell modeling environment
GHSV	gas hour space velocity
GTL	gas-to-liquid
HCN	hydrogen cyanide
HGF	Helmholtz Association of German Research Centres (ger.: Helmholtz-Gemeinschaft Deutscher Forschungszentrum)
HiL	hardware in the loop
HT-PEFC	high-temperature polymer electrolyte fuel cells
HZB	Helmholtz Centre Berlin (ger.: Helmholtzzentrum Berlin)
ICP-OES	inductively coupled plasma optical emission spectrometry
IEF-1	Institute of Energy Research – Materials Synthesis and Processing (ger.: Institut für Energieforschung – Werkstoffsynthese und Herstellungsverfahren)
IEF-2	Institute of Energy Research – Microstructure and Properties of Materials (ger.: Institut für Energieforschung – Werkstoffstruktur und Eigenschaften)
IEF-3	Institute of Energy Research – Fuel Cells (ger.: Institut für Energieforschung – Brennstoffzellen)
IGCC	integrated gasification combined cycle
IGSWEEP-JÜL	Jülich process for application in zero-CO_2 power plants
IQ-BZ	Fuel Cell Qualification Initiative (ger.: Initiative Qualifizierung Brennstoffzelle)
IR	infrared
ISEA	Institute for Power Electronics and Electrical Drives, RWTH Aachen University (ger.: Institut der Stromtrichtertechnik und Elektrische Antriebe der Rheinisch-Westfälischen Universität Aachen)
ITM	trademark name for a steel produced by Plansee
JuMOVe 2	Jülich methanol-operated vehicle
KWKG	German law on combined heat and power (ger.: Kraft-Wärmekopplungsgesetz)
LabView	laboratory virtual instrumentation engineering workbench
LA-ICP-MS	laser ablation inductively coupled plasma mass spectrometry
LargeSOFC	EU project “Large SOFC Systems”
LEL	lower explosive limit
LHSV	liquid hour space velocity

LPPS-TF	low-pressure plasma spray thin film
LSFC	lanthanum-strontium-ferrite cobaltite cathodes
LSM	lanthanum strontium manganese oxide: $La_{0.65}Sr_{0.3}MnO_3$
MALDI-MS	matrix-assisted laser desorption ionization mass spectrometry
MATLAB	programming language for technical calculations
MCFC	molten carbonate fuel cell
MEA	membrane electrolyte assembly
MEMBRAIN	HGF project for CO_2 separation using membranes
METPORE	BMWi project for CO_2 separation using membranes
MT	magnetic tomography
NIP	National Innovation Program
NOW	National Organization for Hydrogen and Fuel Cell Technology Berlin (ger.: Nationale Organisation Wasserstoff- und Brennstoffzellentechnologie Berlin)
NRC	National Research Council
ODE	ordinary differential equations
OXICOAL-AC	BMWi project for CO_2 separation using membranes
OXYMEM	BMWI project for CO_2 separation using membranes
PAFC	phosphoric acid fuel cell
PCCS	photon cross correlation spectroscopy
PD	lecturer (ger.: Privatdozent)
PE	polymer electrolyte
PEFC	polymer electrolyte fuel cell
PEMFC	polymer electrolyte membrane fuel cell
PRO/II	program for simulating process engineering systems and power plants
ProMiNat	academy for students in Dortmund
PSCF	praseodymium-containing perovskite
PTFE	polytetrafluroethylene
PVD	physical vapor deposition
QA	quality assurance
QAS	quality assurance system
R&D	research and development
RAG	company name (ger:: Ruhrkohle Aktiengesellschaft)
Real-SOFC	EU project
RFID	radio frequency identification
RS	reactive sputtering
RTP	rapid thermal processing
RuN-PEM	X-ray-based and neutron-based test methods for PEM fuel cells (ger.: Röntgen- und neutronenbasierte Untersuchungsmethoden für PEM-Brennstoffzellen)
RWTH	RWTH Aachen University (ger.: Rheinisch-Westfälische Technische Hochschule Aachen)
SCT	segmented cell technology
SEM	scanning electron microscope
SGL	Company originated from a merger between SIGRI GmbH and Great Lakes Carbon

Sigraflex	expanded natural graphite manufactured by SGL
SIMS	secondary ion mass spectrometry
Simulink	software for system modeling
SLEIPNER	norwegian project
SLM	selective laser melting
SOFC	solid oxide fuel cell
SPP	steam power plant
SPS	software-programmed control mechanisms (ger.: Software-programmierte Steuerung)
SRMS	spatially resolved mass spectrometry
TERS	tip-enhanced Raman scattering
TG	thermogravimetrical analysis
TGA	thermogravimetry analyzer
TPD	temperature-programmed desorption
TPO	temperature-programmed oxidation
TPR	temperature-programmed reduction
u_F	fuel utilization rate
VBZ	fuel cell process engineering
WBzU	Fuel Cell Education and Training Centre, Ulm (ger.: Weiterbildungszentrum Brennstoffzelle Ulm)
WHG	Water Resources Act (ger.: Wasserhaushaltsgesetz)
XRF	X-ray fluorescence analysis

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ISBN 978-3-89336-553-1

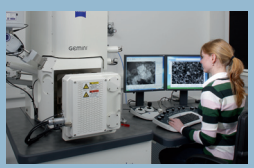
27. **IEF-3 Report 2009. Grundlagenforschung für die Anwendung**
(2009), ca. 223 Seiten
ISBN: 978-3-89336-554-8

Institute of Energy Research – Fuel Cells (IEF-3)

IEF-3 is one of nine sub-institutes within the Institute of Energy Research at Forschungszentrum Jülich GmbH. IEF-3 aims to conduct research of social, ecological and economic relevance and thus generate groundbreaking results on an international level. This quality of work is achieved through basic research in close coordination with technical development work in relevant scientific and technical fields of expertise. Special significance is attached here to international cooperations with partners from research and industry.

By implementing research results in innovative products, procedures and processes in cooperation with industry, IEF-3 hopes to help bridge the gap between science and technology. Cooperation with universities, universities of applied sciences, training departments and training centers is designed to promote opportunities for further education and training.

With a staff of approximately 100, IEF-3 concentrates on the basic topics of electrochemistry and process engineering for fuel cells. In an integrated approach, the four key areas worked on in the institute – direct methanol fuel cells, high-temperature polymer electrolyte fuel cells, solid oxide fuel cells and fuel processing systems – are accompanied by systems analysis and theoretical investigations, basic modeling and simulations, and by experimental and theoretical systems evaluations. The information generated in these areas is used to design and verify functional systems. In addition, particular attention is given to the development, configuration and application of special measuring techniques for the structural analysis of membrane electrode assemblies, for flow simulation and visualization, and for the characterization of stacks.



The field emission scanning electron microscope (FE-SEM) with integrated energy dispersive X-ray spectroscope (EDX) is the most important instrument in the physico-chemical fuel cell laboratory for imaging MEA structures on a nanoscale.

The section of the fuel store pictured here shows a 25-m^3 tank together with two 2-m^3 tanks which are used to store and supply kerosene as well as a large number of other fuels stemming from middle distillates.

This flexible line coater is the central processing instrument in the fabrication facility. It allows different coating and further processing steps to be conducted for the fabrication of electrodes on gas diffusion layers, transfer films and membranes.

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JÜLICH
FORSCHUNGSZENTRUM